

Organic Chemistry Part 2

CHAPTER 3

Alkyl and Aryl Halides

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3

Alkyl and Aryl Halides

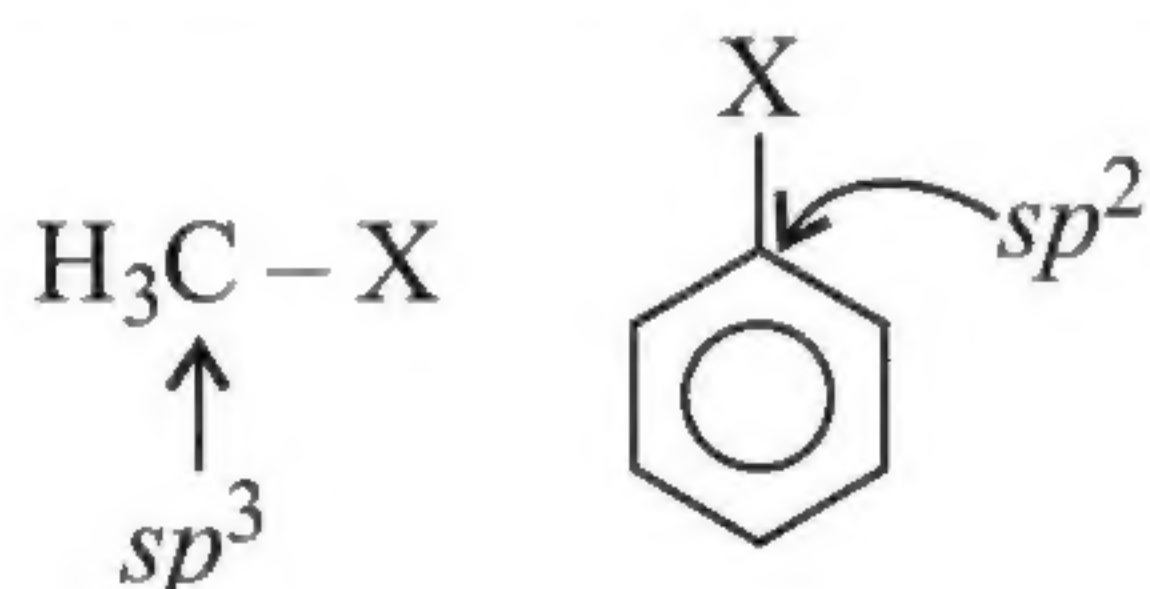
3.1 INTRODUCTION

Alkyl halides (RX) and aryl halides (ArX) are obtained by replacement of H atom(s) by halogen atom(s) from aliphatic or aromatic hydrocarbons.

a. General formula:

Monohaloalkane	$C_nH_{2n+1}.X$	(X = F, Cl, Br, I)
Dihaloalkane	$C_nH_{2n}.X_2$	
Monohaloarenes	$C_6H_5.X$	
Dihaloarenes	$C_6H_4.X_2$	

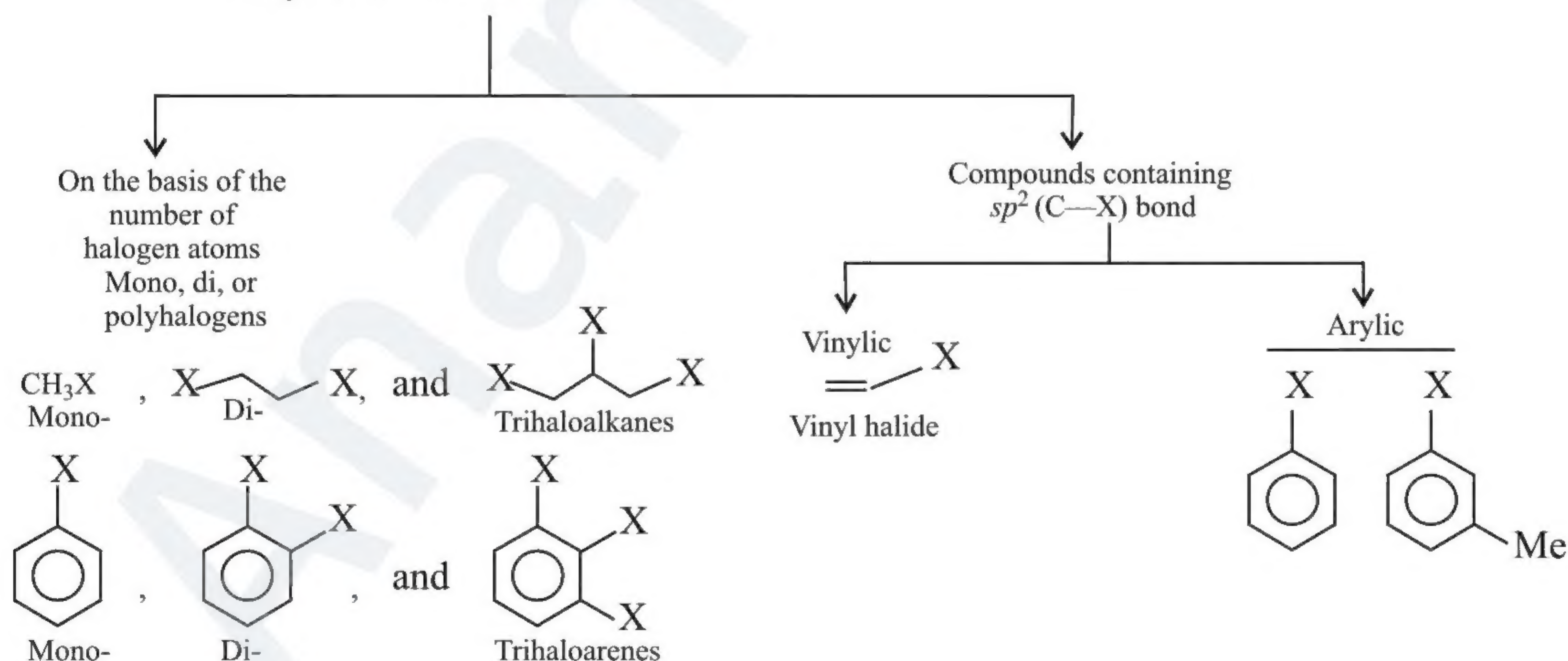
The X in an alkyl halide is bonded to an sp^3 -hybridised C of any alkyl group, whereas in aryl halide, X is bonded to sp^2 -hybridised C atom of an aryl group.



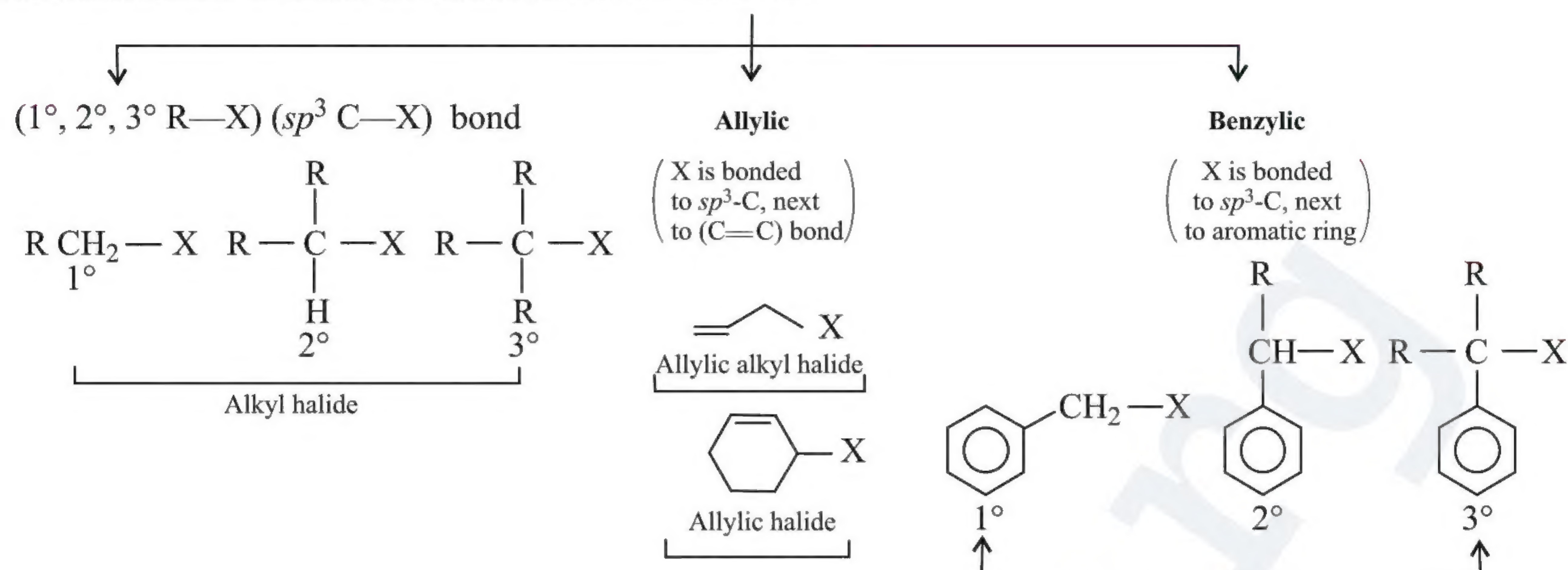
b. Uses: They occur in nature and are used as solvents for relatively non-polar compounds. They are widely used in the synthesis of various clinically useful compounds, e.g., antibiotic, Chloromycetin (for the treatment of typhoid fever), Chloroquine (for the treatment of malaria), Halothane ($F_3C-CHClBr$) and C_2H_5Cl (used as local anaesthetic during surgery), and certain fully fluorinated compounds (as potential blood substitutes in surgery). Freons are used as refrigerants and DDT is used as an insecticide. CCl_4 is used as fire extinguisher under the name 'pyrene' and is also a popular solvent for dry cleaning.

c. Classification

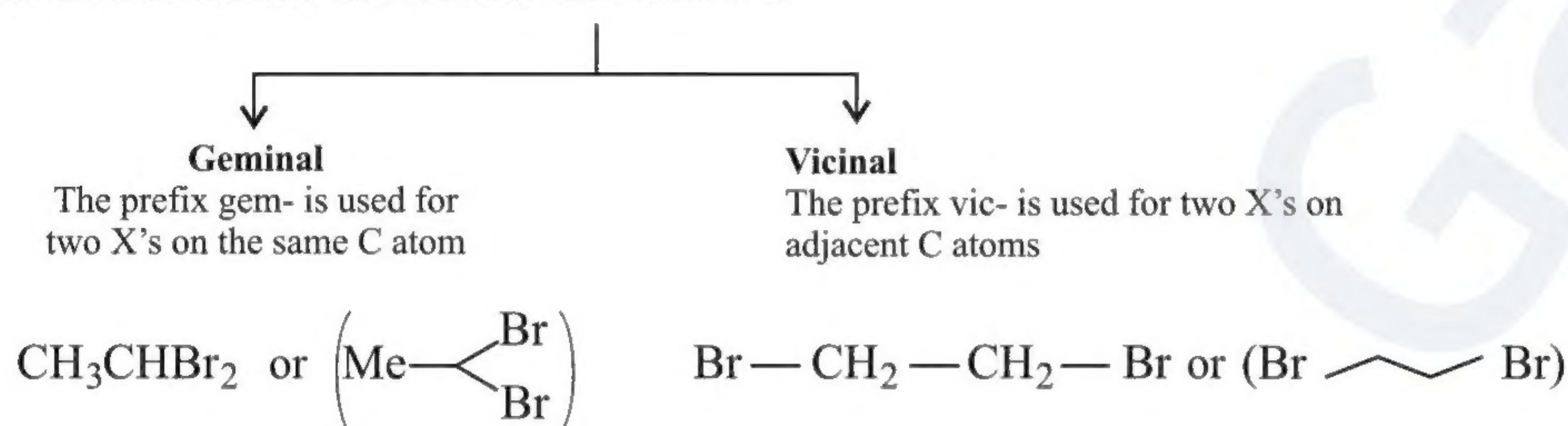
I. They are classified as follows:



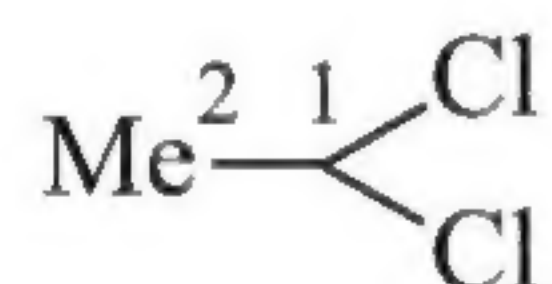
II. Monohaloalkanes or arenes are further classified as follows:



III. Dihaloalkanes are classified as follows:

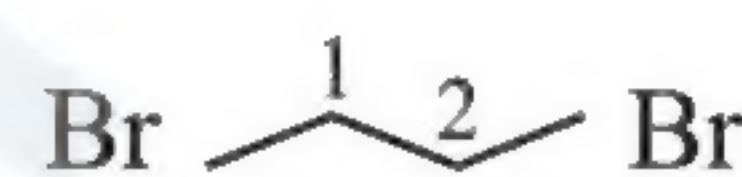


In common name (C.N.) system, gem-dihalides are named as **alkylidene halides** and vic-dihalides are named as **alkylene dihalides**, e.g.,



C.N: Ethylidene chloride (gem-dihalide)

IUPAC name: 1,1-Dichloro ethane



C.N.: Ethylene dibromide (vic-dihalide)

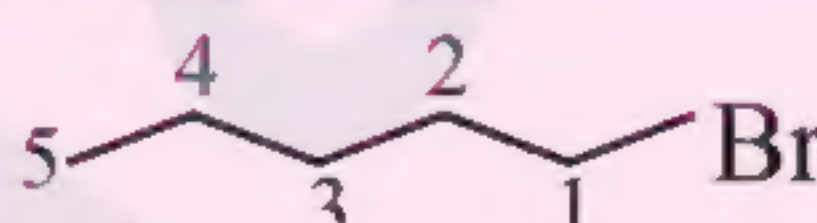
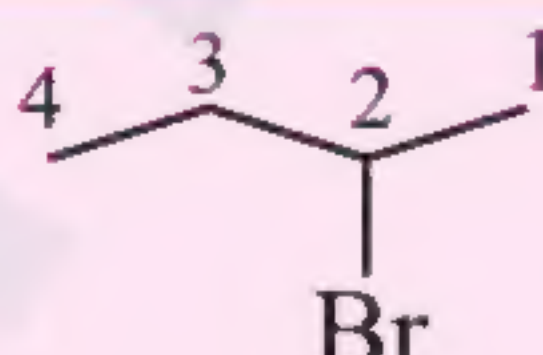
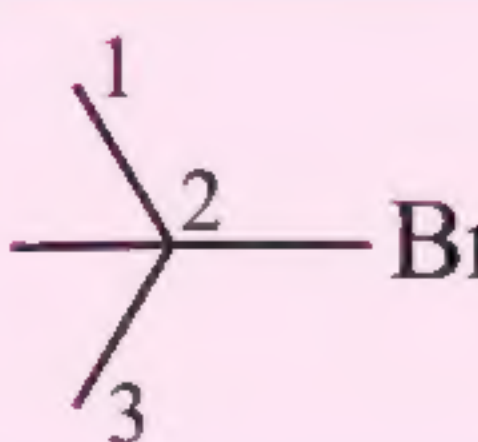
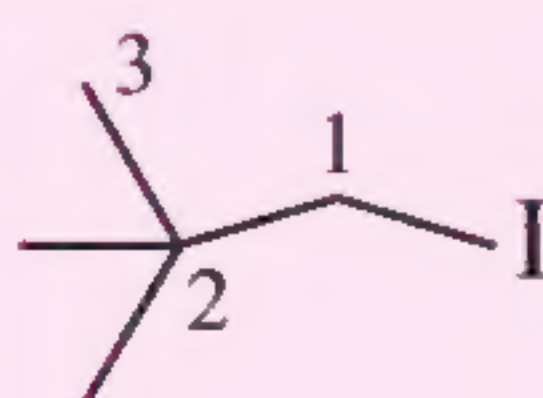
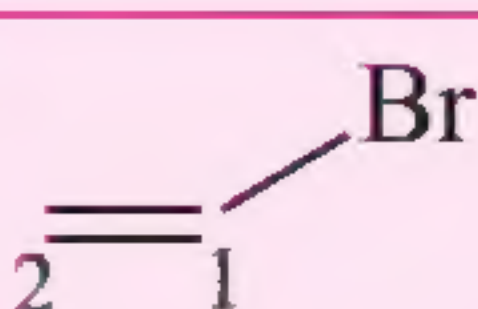
IUPAC name: 1,2-Dibromo ethane

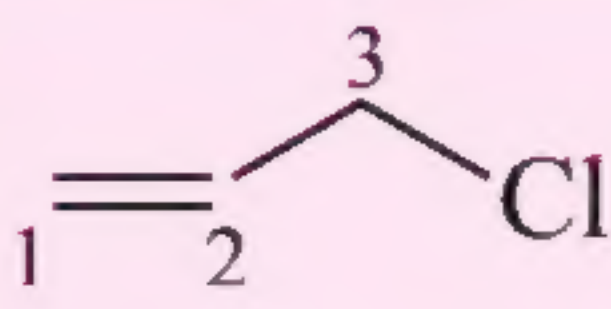
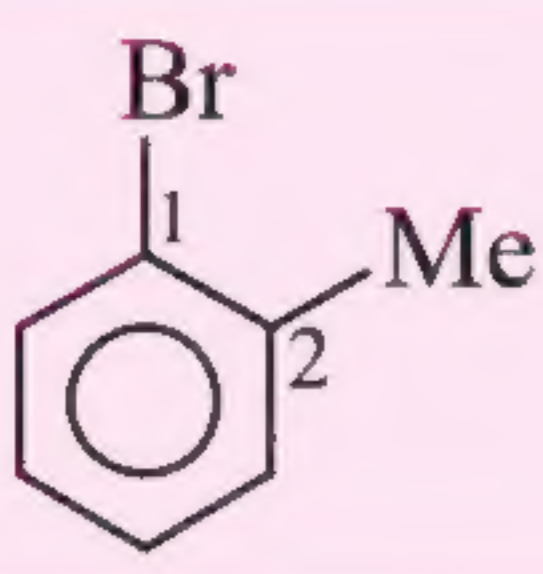
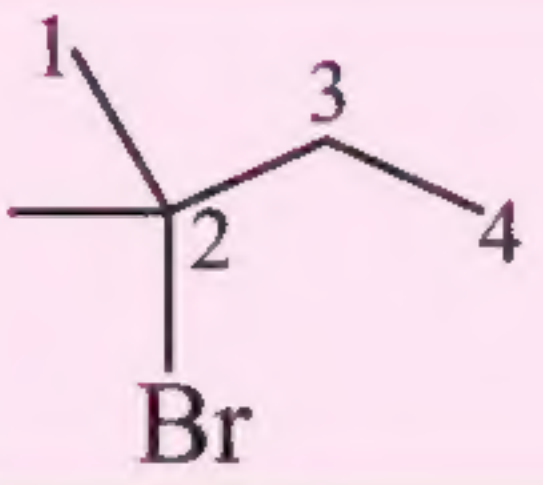
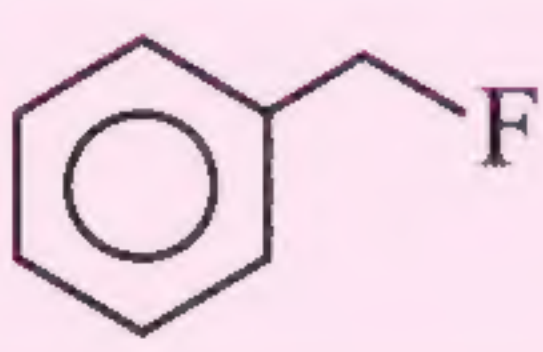
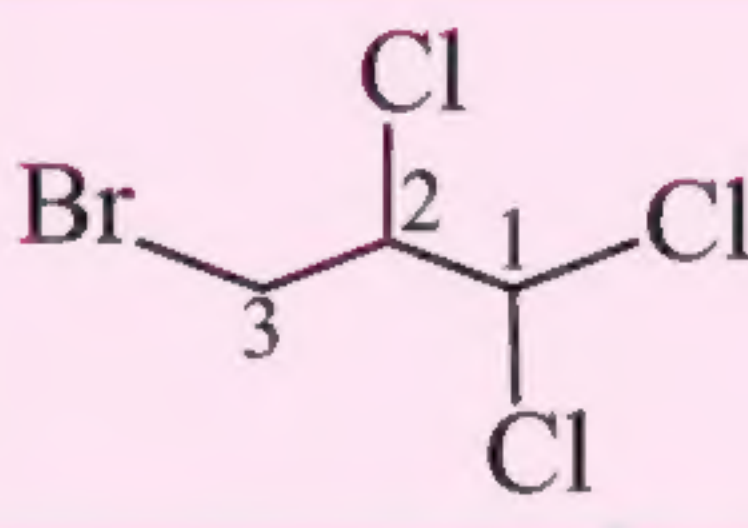
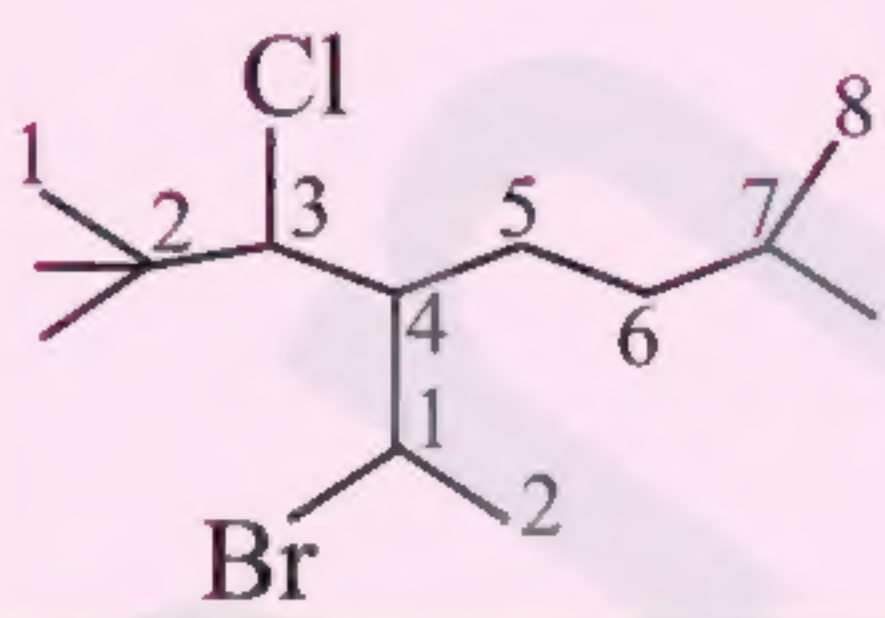
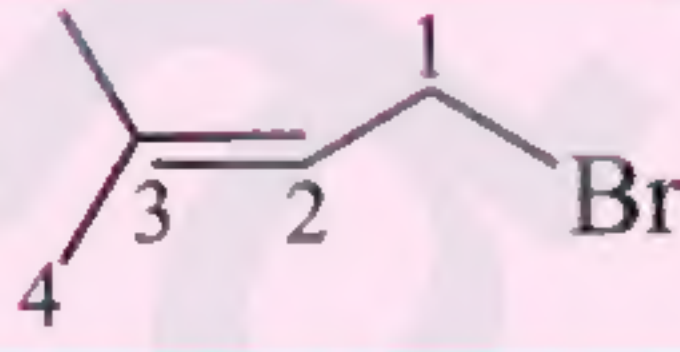
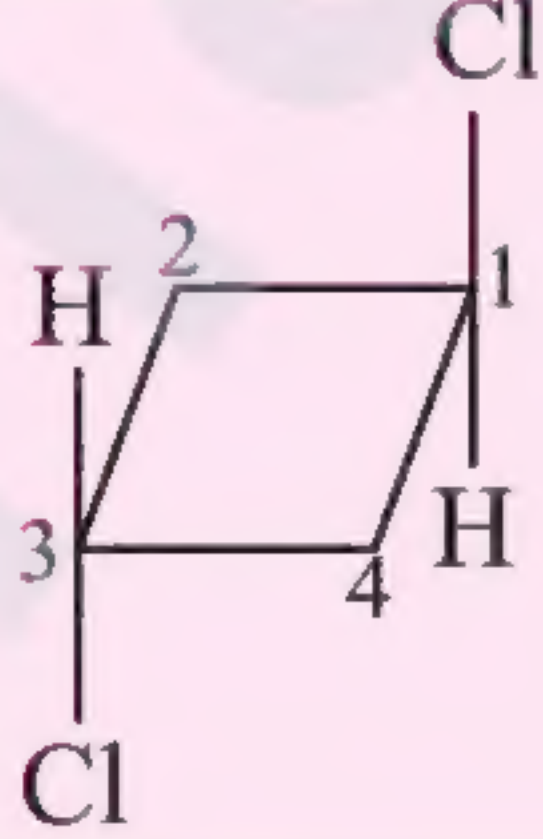
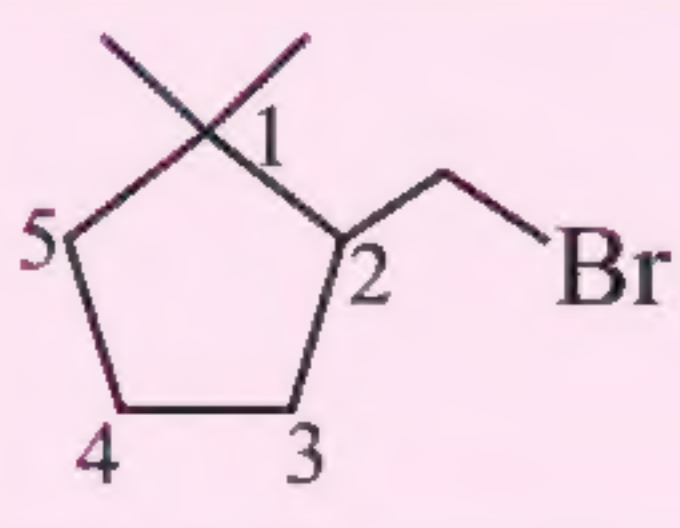
3.2 NOMENCLATURE

In IUPAC system, alkyl halides are named as haloalkanes. The longest chain is numbered so that the smallest numbers are used to indicate the positions of the substituent, and different substituents are named alphabetically.

In common name system, the alkyl group name is followed by the halide name, e.g., CH_3Cl (methyl chloride).

Table 3.1 IUPAC and common names of some R—X and Ar—X

S.No.	Condensed formula	Bond line formula	IUPAC name	Common name
1.	$CH_3(CH_2)_4 \cdot Br$ 1°RX		1-Bromo pentane	<i>n</i> -Amyl bromide
2.	$C_2H_5CH Br CH_3$ or Et CHBr Me 2°RX		2-Bromo butane	<i>sec</i> -Butyl bromide
3.	$(CH_3)_3C Br$ or $Me_3C Br$ 3°RX		2-Bromo-2-methyl butane	<i>tert</i> -Butyl bromide
4.	$(CH_3)_3C CH_2I$ 1°RX		1-Iodo-2,2-dimethyl propane	<i>neo</i> -Pentyl iodide
5.	$CH_2=CHBr$ Vinylic		1-Bromo ethene	Vinyl bromide

6.	$\text{CH}_2=\text{CHCH}_2\text{Cl}$ Allylic		3-Chloro propene	Allyl chloride
7.	CH_2Br_2 (gem-)	—	1,1-Dibromo methane	Methylenediene bromide
8.	CHCl_3	—	Trichloro methane	Chloroform
9.	CHBr_3	—	Tribromo methane	Bromoform
10.	$\text{CH}(\text{NO}_2)_3$	—	Trinitro methane	Nitroform
11.	CHF_3	—	Trifluoro methane	Fluoroform
12.	CBr_4	—	Tetrabromo methane	Carbon tetrabromide
13.	$o\text{-BrC}_6\text{H}_4\text{Me}$		1-Bromo-2-methyl benzene or 2-Bromotoluene	<i>o</i> -Bromo toluene
14.	Me_2CBrEt		2-Bromo-2-methyl butane	<i>tert</i> -Amyl bromide
15.	PhCH_2F		Fluorophenyl methane	Benzyl fluoride
16.	$\text{BrCH}_2\text{CHClCHCl}_2$		3-Bromo-1,1,2-tri-chloropropane	—
17.	$\text{Me}_3\text{CCHClCH}(\text{CHBrMe})$ $(\text{CH}_2)_2\text{CHMe}_2$		4-(1-Bromoethyl)-3-chloro- 2,2,7-trimethyl octane	—
18.	$\text{Me}_2\text{C}=\text{CHCH}_2\text{Br}$		1-Bromo-3-methyl but-2-ene	—
19.	—		<i>trans</i> -1,3-Dichloro cyclobutane	—
20.	—		2-Bromo methyl 1,1-dimethyl cyclopentane	—

3.3 DIPOLE MOMENT

Since the electronegativities (EN) of halogens are more than those of C, so the (C—X) bond is polarised as $\left(\text{>C}^{+\delta}-\text{X}^{-\delta}\right)$, and hence

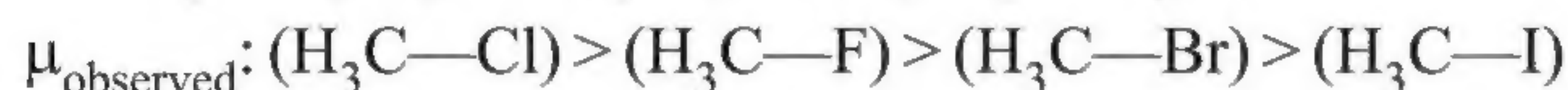
RX and ArX show dipole moment (μ).

$$\mu = q \times d [q = \text{charge}, d = \text{distance between the (C—X) bond}]$$

More the EN of halogen, more is the polarisation of the (C—X) bond and thus greater are the charges on (C^{+δ}—X^{−δ}). EN of halogens: F > Cl > Br > I.

As the size of halogens increases, the bond length of the (C—X) bond increases.

The order of bond length of (C—X) bond:



μ of (H₃C—Cl) is higher than that of (H₃C—F), due to the combined effect of charge and bond length. EN difference between F and Cl is small, therefore, μ of (H₃C—Cl) is higher than that of (H₃C—F). It explains that the bond length of the (C—Cl) bond is more predominant than charge factor.

EN difference between F and Br or I is much more than the bond length difference in them. Therefore, in (C—Br) and (C—I), the charge factor is more predominant than bond length factor.

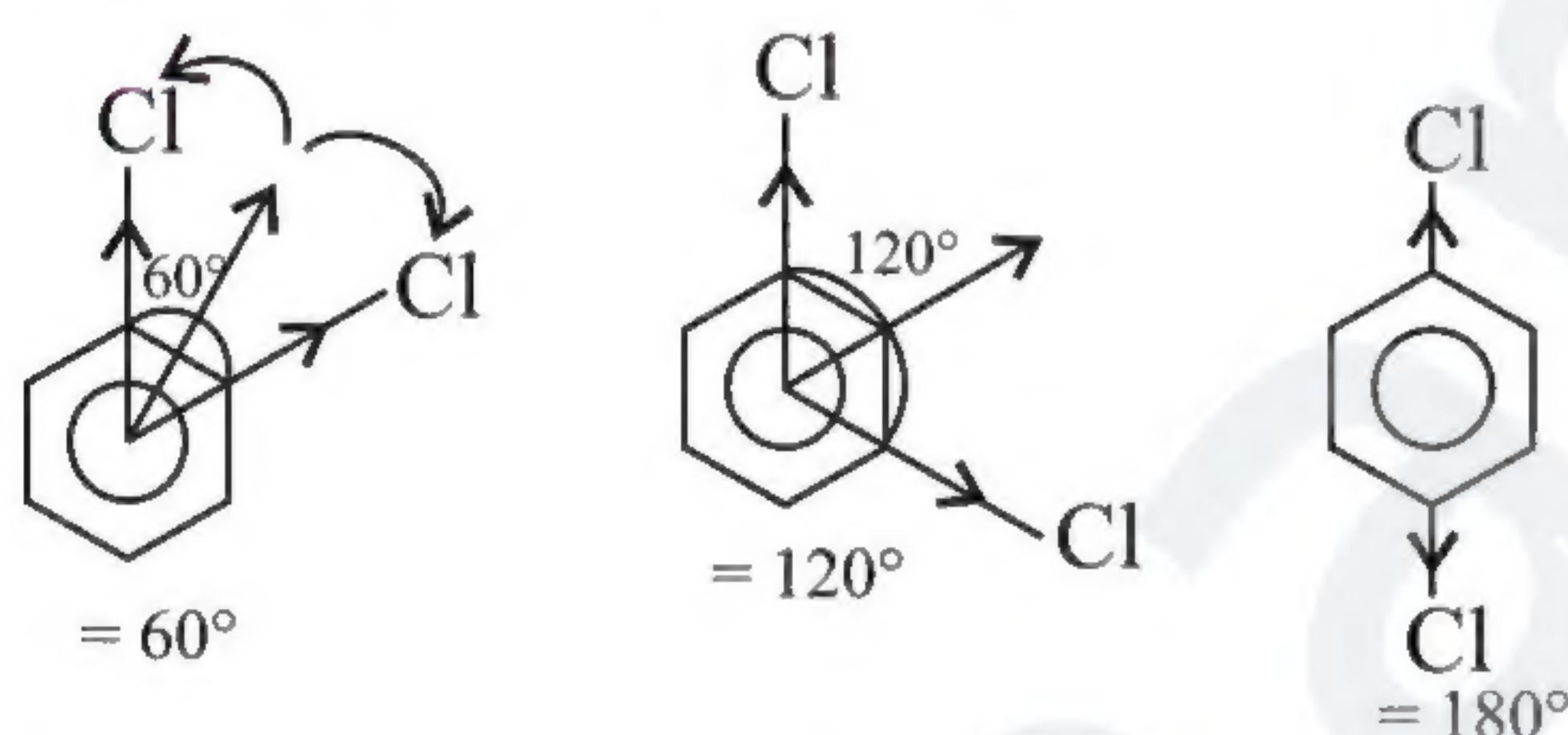
Table 3.2 EN of X, (C—X) bond lengths, bond enthalpies and dipole moments

	Bond	EN*	Bond length (pm)	Bond enthalpies (kJ mol ^{−1})	μ (Debye)
1.	H ₃ C—F	F = 4	139	452	1.82
2.	H ₃ C—Cl	Cl = 3.2	178	351	1.94
3.	H ₃ C—Br	Br = 3.0	193	293	1.79
4.	H ₃ C—I	I = 2.7	214	234	1.64

* EN values are measured by Pauling scale.

3.3.1 DIPOLE MOMENT MEASUREMENT METHOD

Dipole moment: *o*- > *m*- > *p*-Dichlorobenzene



Dipole moment (μ) is given by:

$$\mu = 2\mu_{C-Cl} \cos\left(\frac{\theta}{2}\right)$$

where μ_{C-Cl} is the vector moment and θ is the angle between two vector moments.

$$\text{Thus, } \mu \propto \cos\left(\frac{\theta}{2}\right) \text{ or } \mu \propto \frac{1}{\theta}$$

Hence, smaller the value of θ , greater is the value of the dipole moments. But due to dipole-dipole repulsion, there are some differences in the experimental and theoretical values of μ .

For example, μ calculated and μ observed for *o*-dichlorobenzene, respectively, are 6.30 D and 6.00 D.

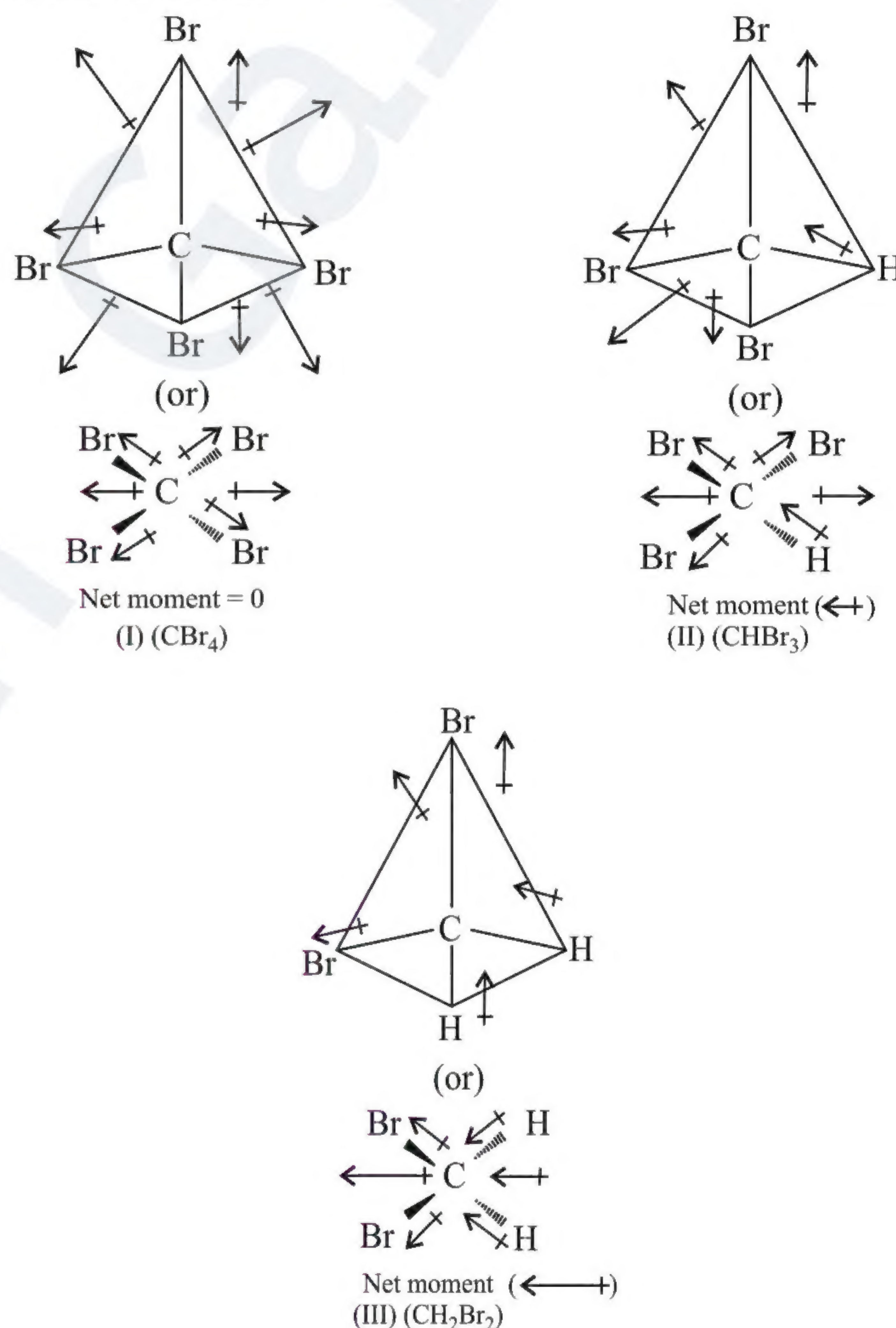
Due to dipole-dipole repulsion of two Cl atoms, θ increases and μ decreases.

ILLUSTRATION 3.1

Arrange the following compounds in decreasing order of dipole moment values. Explain the order.

- I. CBr₄ II. CHBr₃ III. CH₂Br₂ IV. CH₃Br

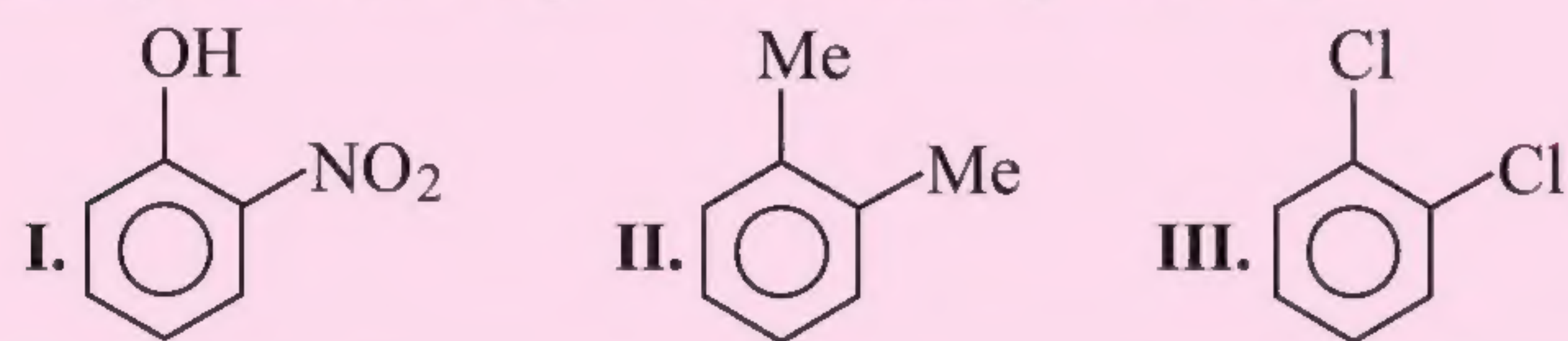
Sol. The three-dimensional structures of three compounds along with the direction of dipole moments in each of their bonds are shown as below:



- I. CBr₄ is symmetrical and therefore has $\mu = 0$.
- II. CHBr₃, the resultant of two (C—Br) dipoles, is opposed by the resultant of (C—H) and (C—Br) bonds, which is smaller than the former. Therefore, (CHBr₃) shows $\mu = 1.01$ D.
- III. CH₂Br₂, the resultant of two (C—Br) dipole moments, is reinforced by two (C—H) bonds; therefore, (CH₂Br₂) shows $\mu = 1.52$, which is higher than that of CHBr₃.
- IV. (CH₃—Br), due to −I effect of Br, has highest μ .
 $\therefore \mu$ order is : (IV) > (III) > (II) > (I).

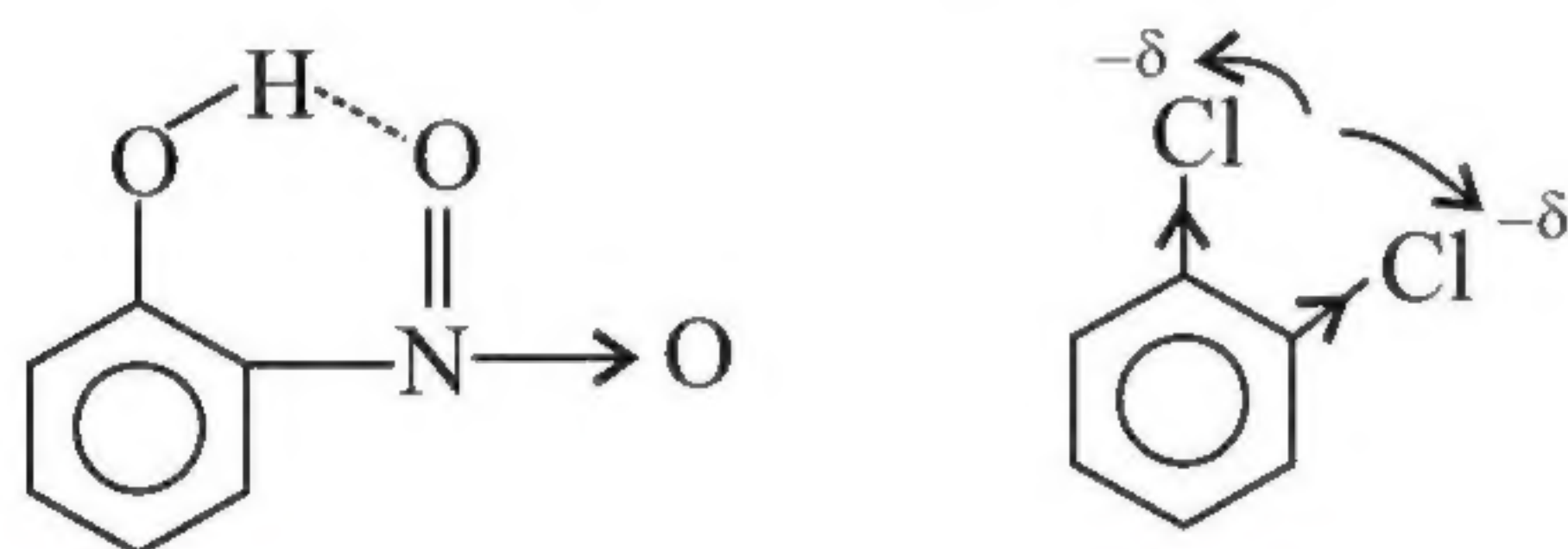
ILLUSTRATION 3.2


Arrange the following in the decreasing order of μ .



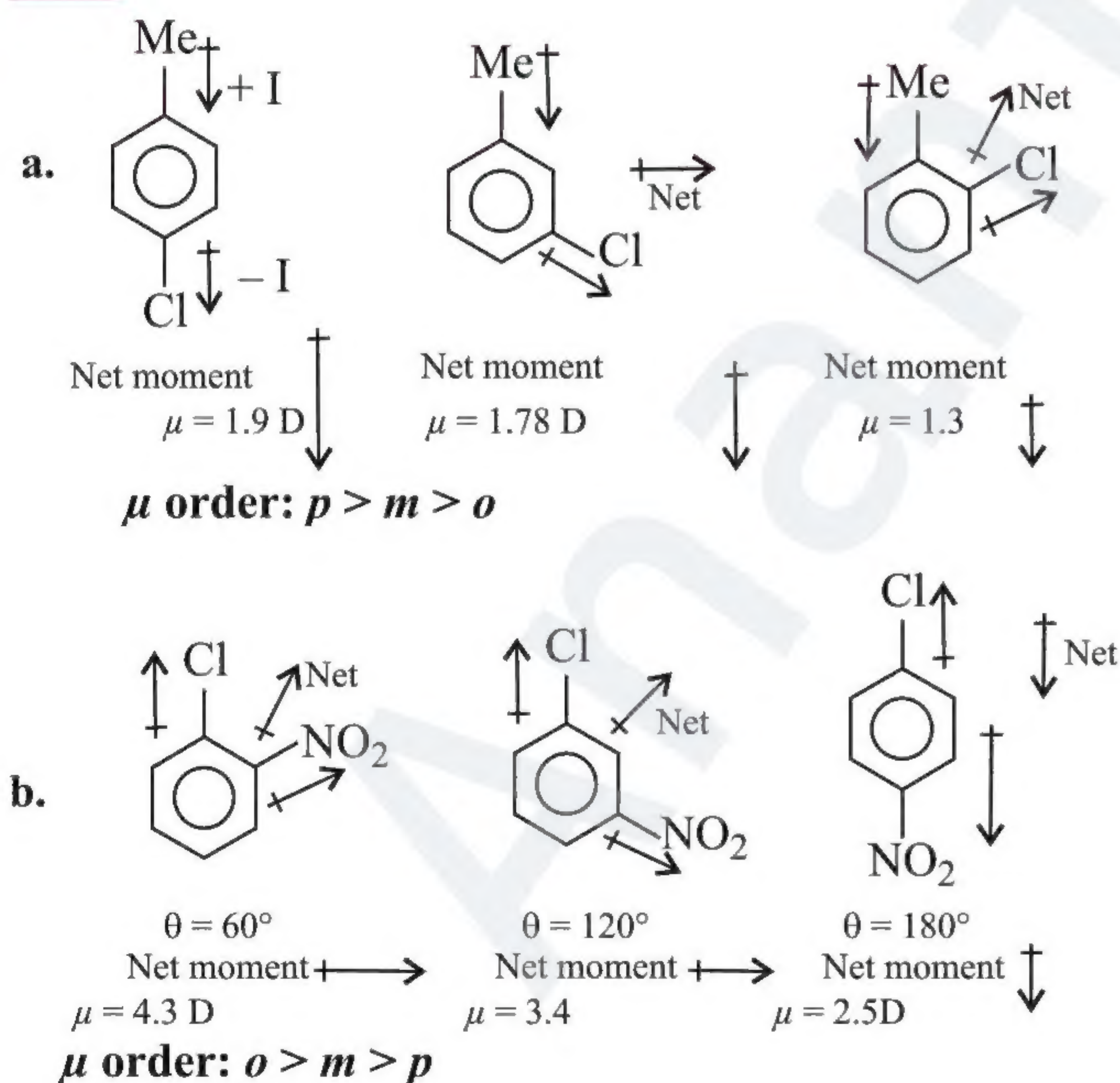
Sol. (I) > (II) > (III).

In case of (I), the intramolecular H-bonding decreases the bond angle ($< 60^\circ$), hence μ is increased. In case of (II), dipole-dipole repulsion of two Cl atoms in *ortho*-position increases the bond angle ($> 60^\circ$), therefore μ is decreased. In (III), bond angle = 60° . Hence the order of μ is (I) > (II) > (III).

**ILLUSTRATION 3.3**

- Assign orientation to the three chlorotoluenes with $\mu = 1.3, 1.78$, and 1.9 D.
- Assign orientation to the three chloronitrobenzenes with $\mu = 2.5, 3.4$, and 4.3 D.
- Which has higher μ : (I) -Br or (II) PhBr?

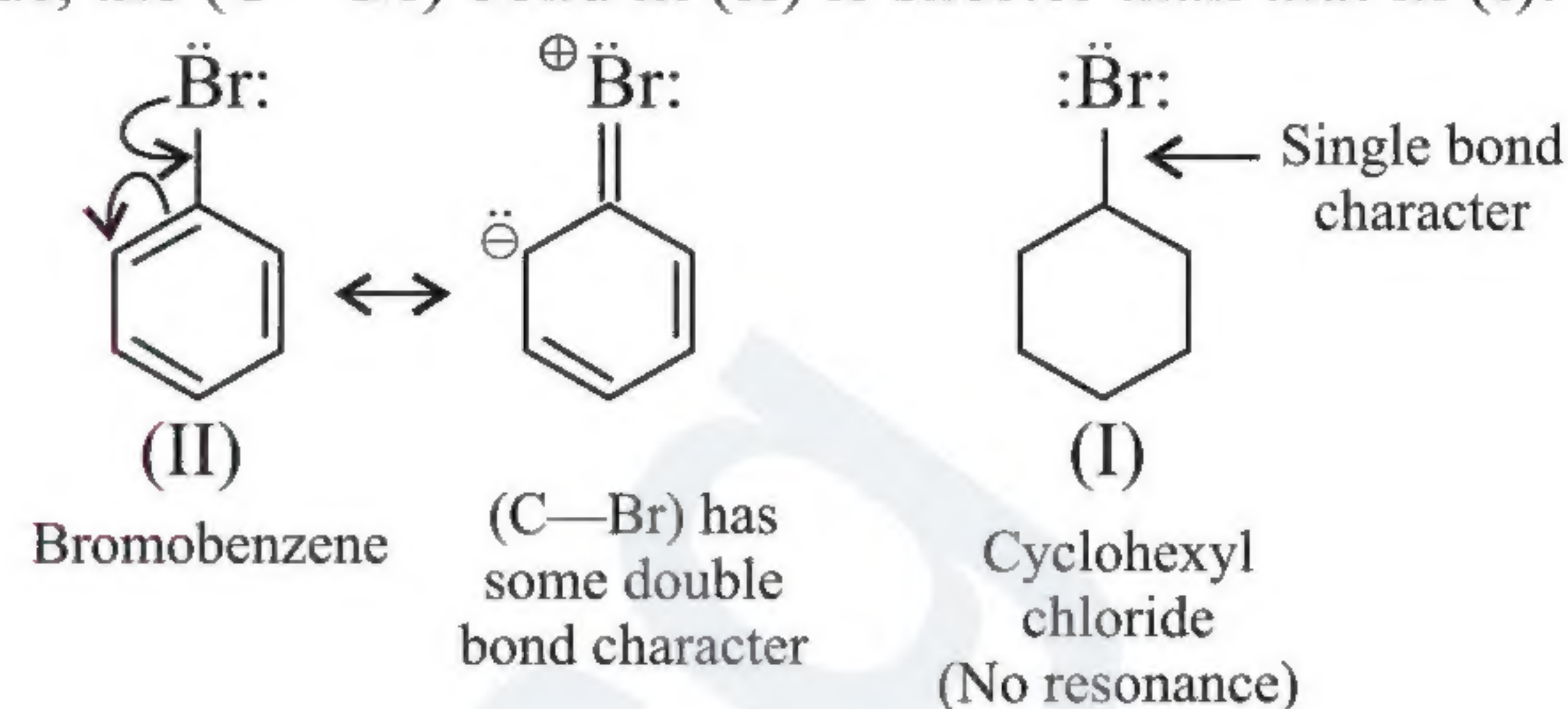
Sol.



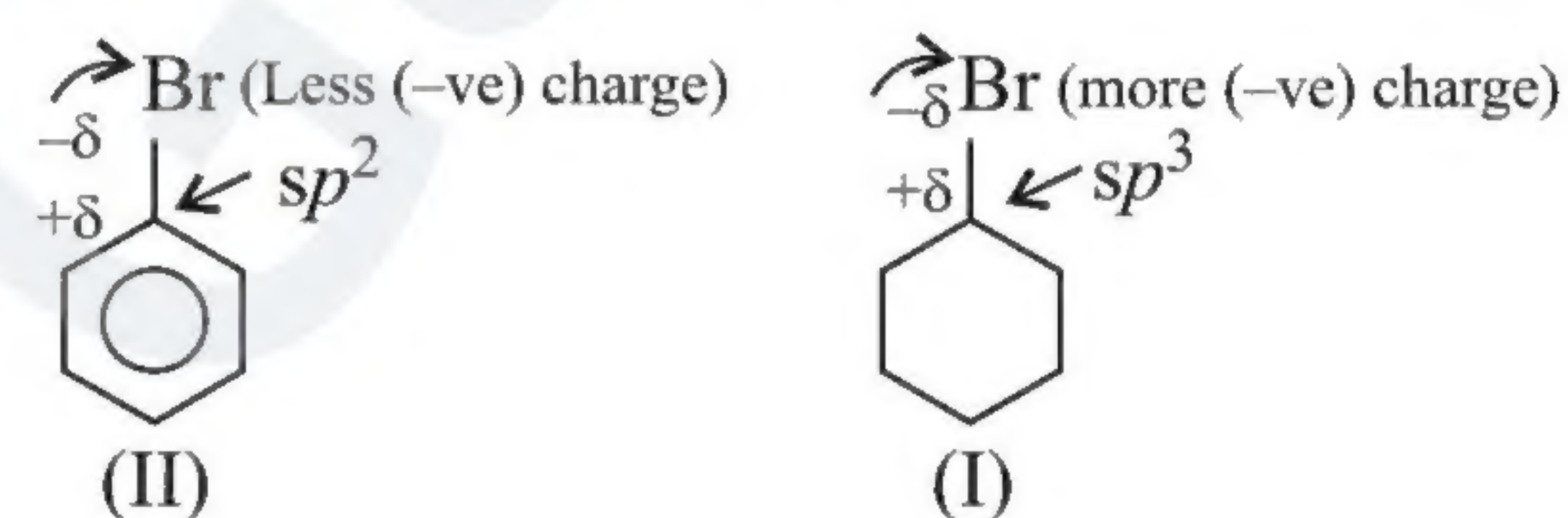
c. μ of (I) > (II)

- Bromobenzene (II) is resonance stabilised due to delocalisation of LP \bar{e} 's of the Br atom in the benzene ring. The (C—Br)

bond acquires some double bond character, which in (I) is a single bond, since it does not undergo resonance. In other words, the (C—Br) bond in (II) is shorter than that in (I).



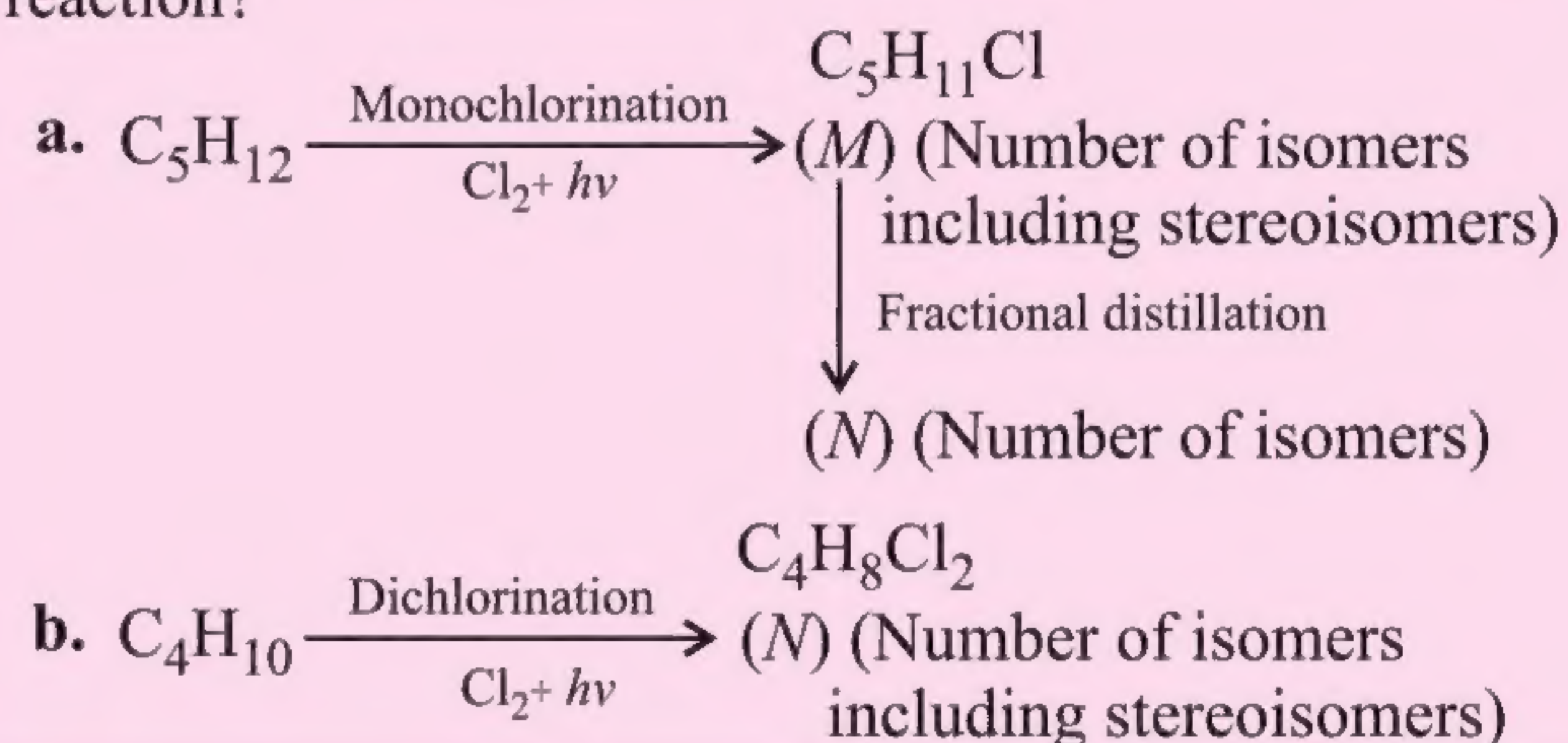
- Due to more s -character, sp^2 -hybridised C is more EN than sp^3 -hybrid C atom; therefore, the sp^2 -hybrid C of the (C—Br) bond in (II) has less tendency to release \bar{e} 's to Br than an sp^3 -hybridised C atom of (I). As a result the (C—Br) bond in (I) is more polar than in (II), i.e., the magnitude of negative charge (δ^-) is more on Br atom of (I) than in (II).



Therefore μ of (I) > (II) [since $\mu = q \times d$ (charge \times distance)].

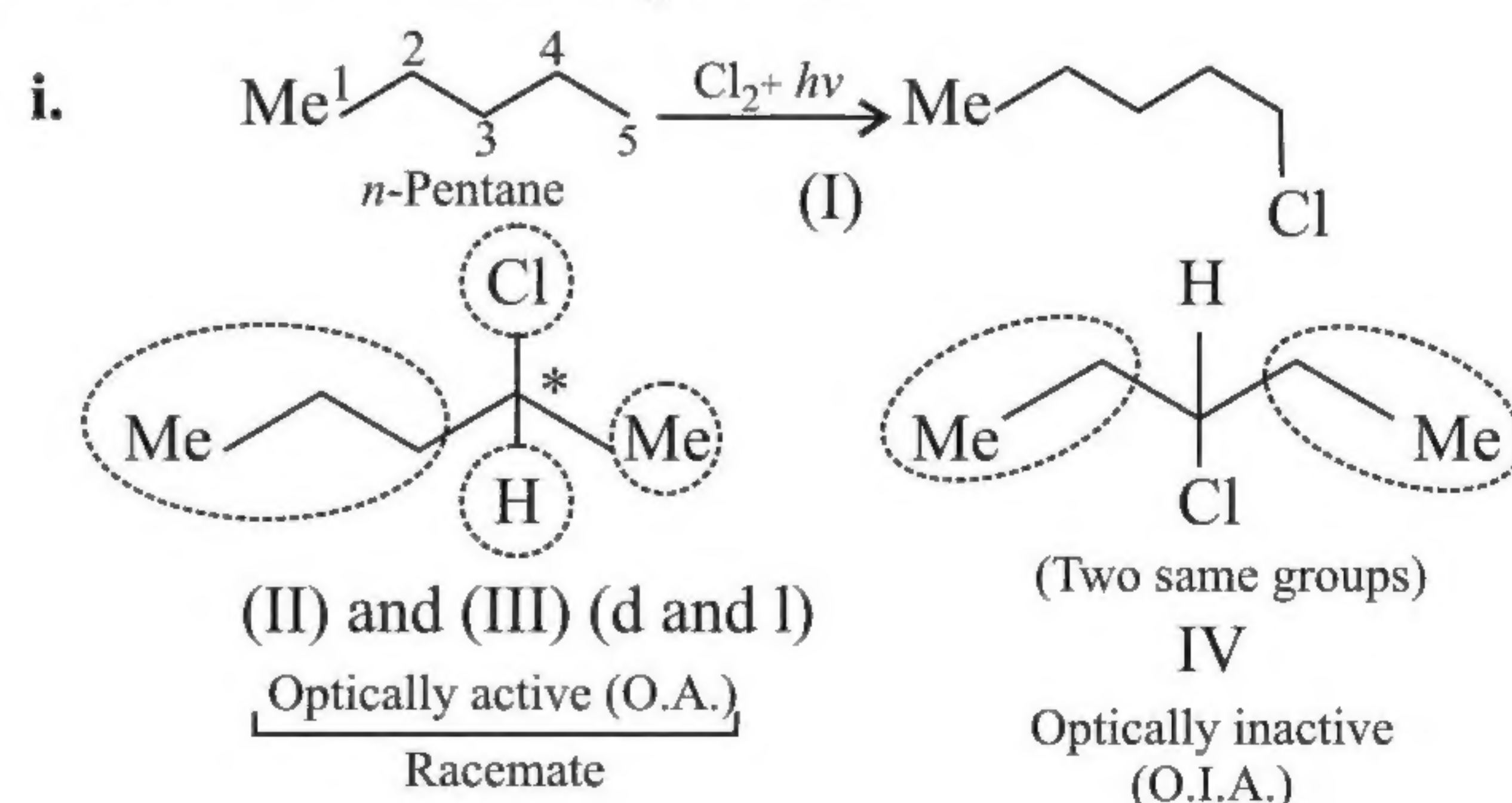
ILLUSTRATION 3.4

What are the numerical values of (M) and (N) in the following reaction?

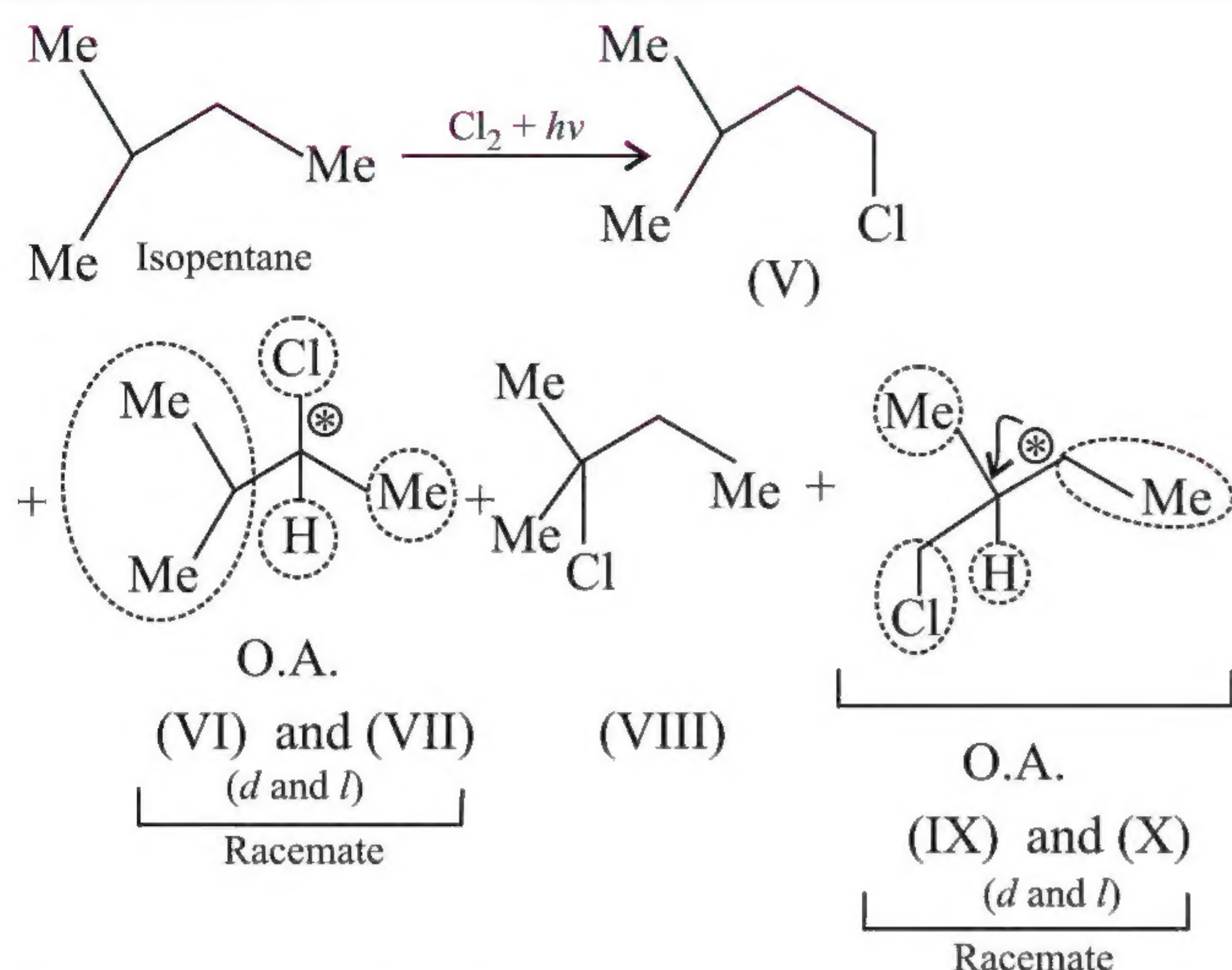


Sol.

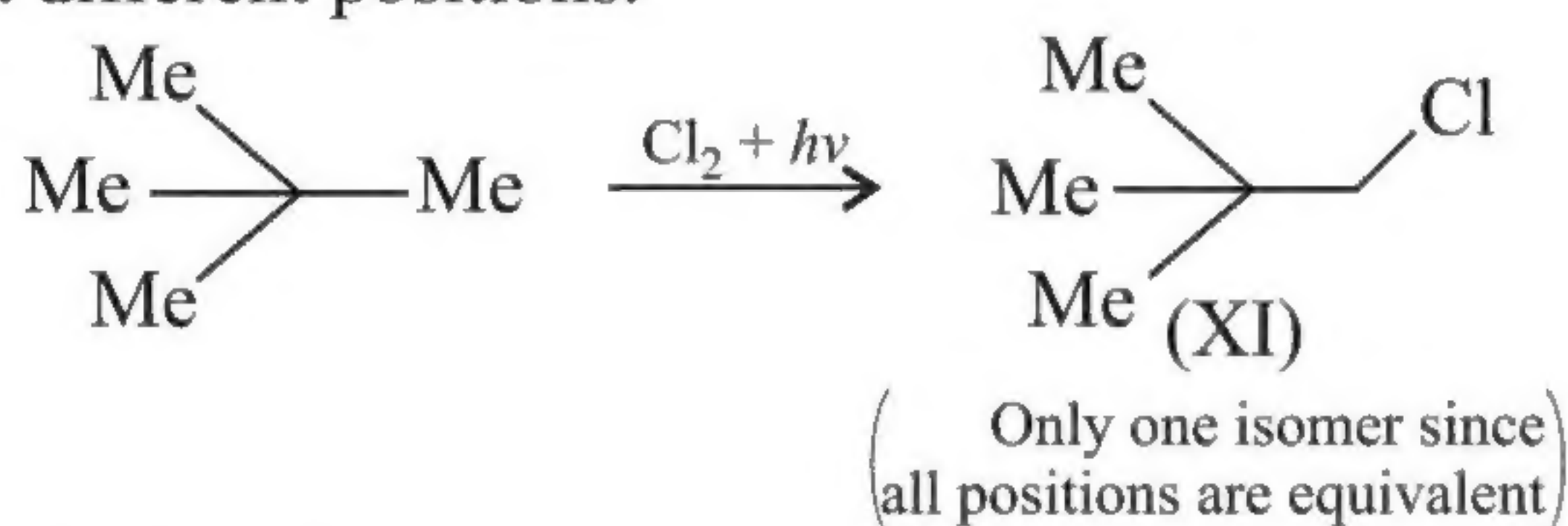
- First, write the straight-chain structures of C_5H_{12} and substitute Cl at different positions.



- Write the branched structure of C_5H_{12} and substitute Cl at different positions.



iii. One isomer of C_5H_{12} is neo-pentane and substitutes Cl at different positions.

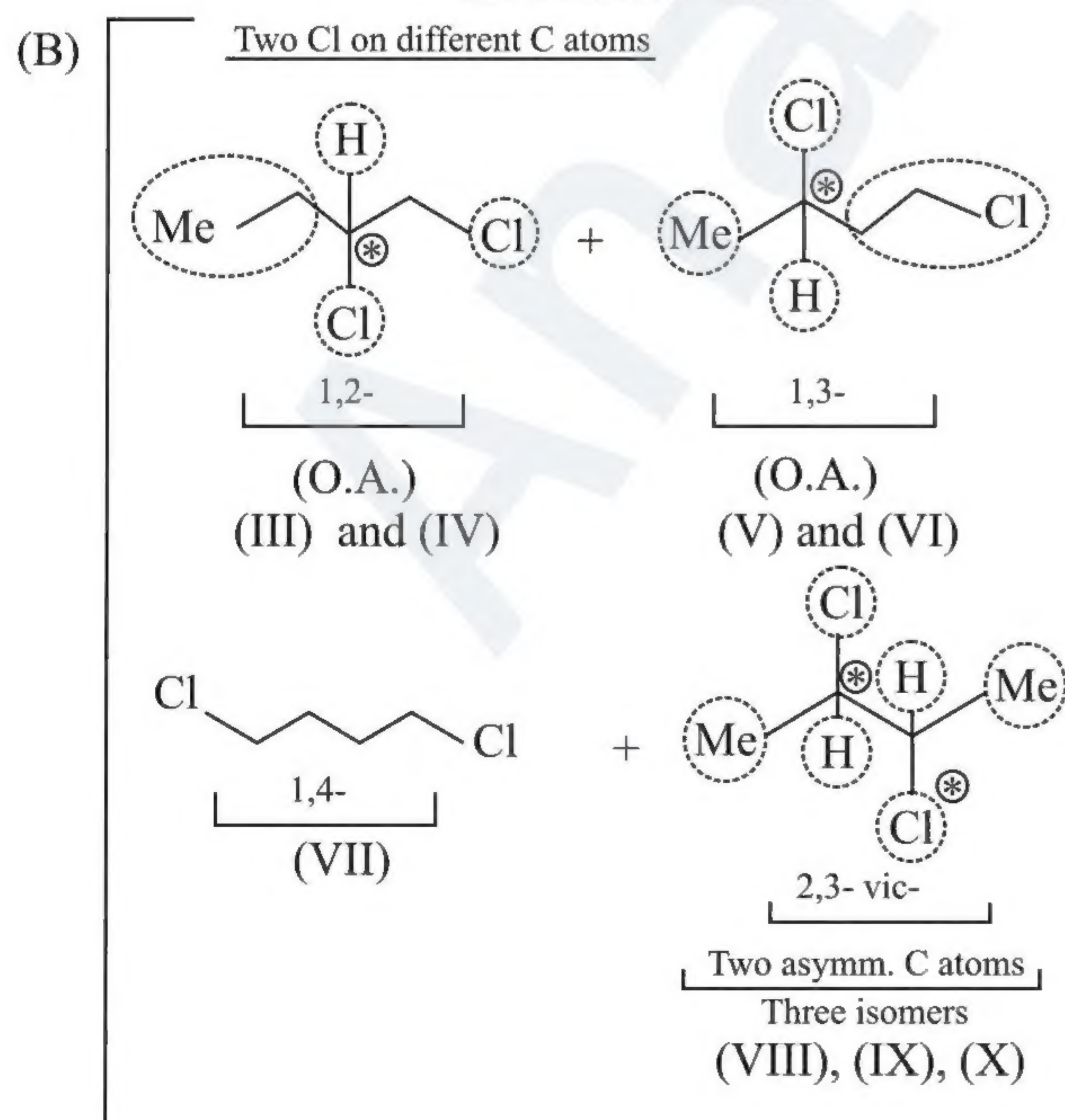
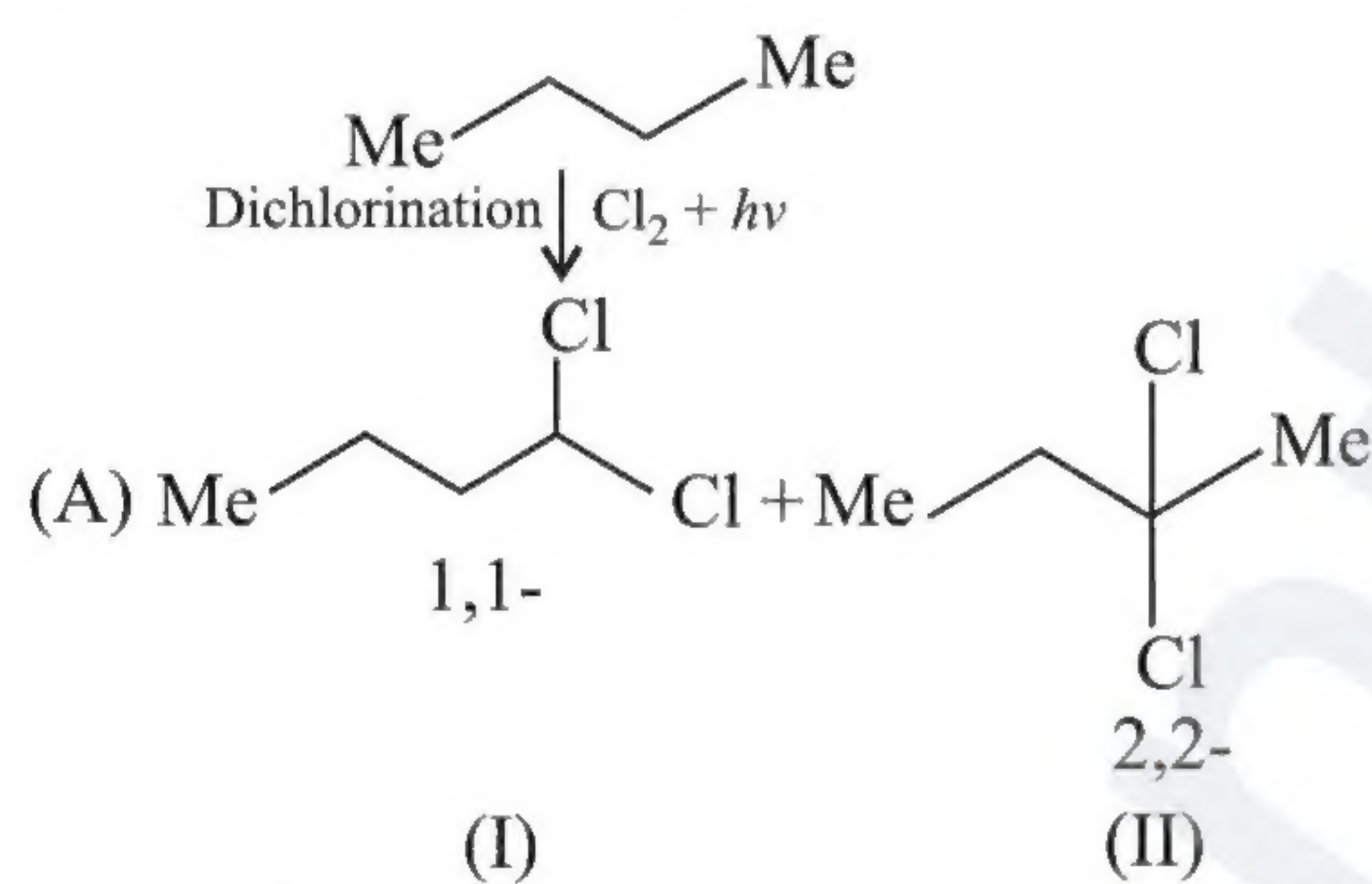


Total isomers of $\text{C}_5\text{H}_{11}\text{Cl}$ (including stereoisomers) = 11
 On fractional distillation, optical isomers would not separate.

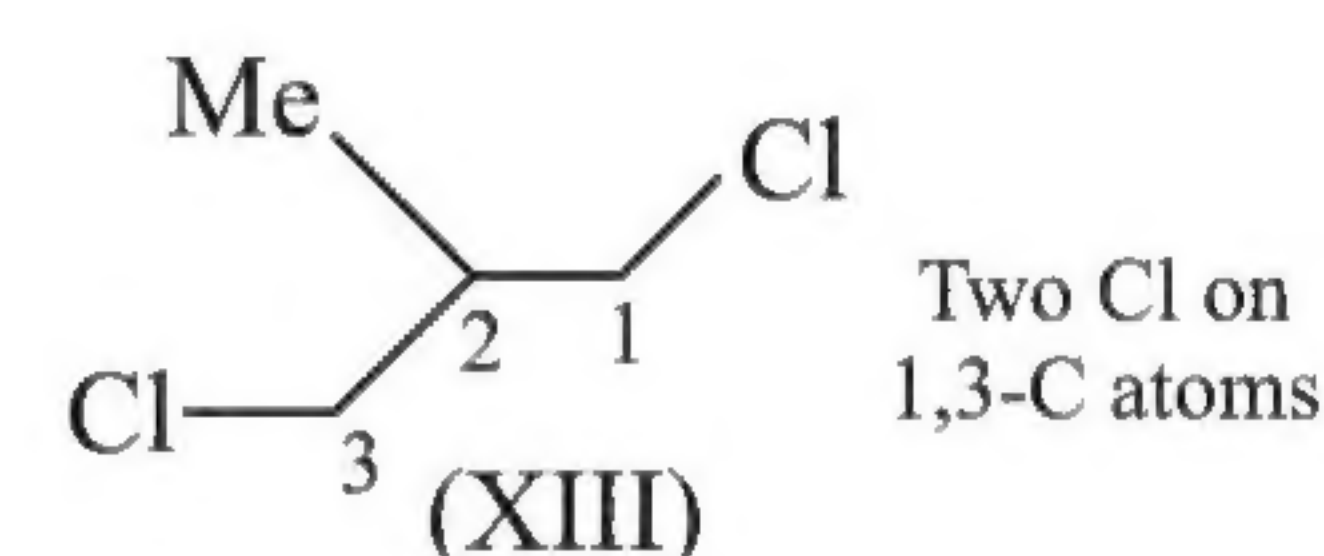
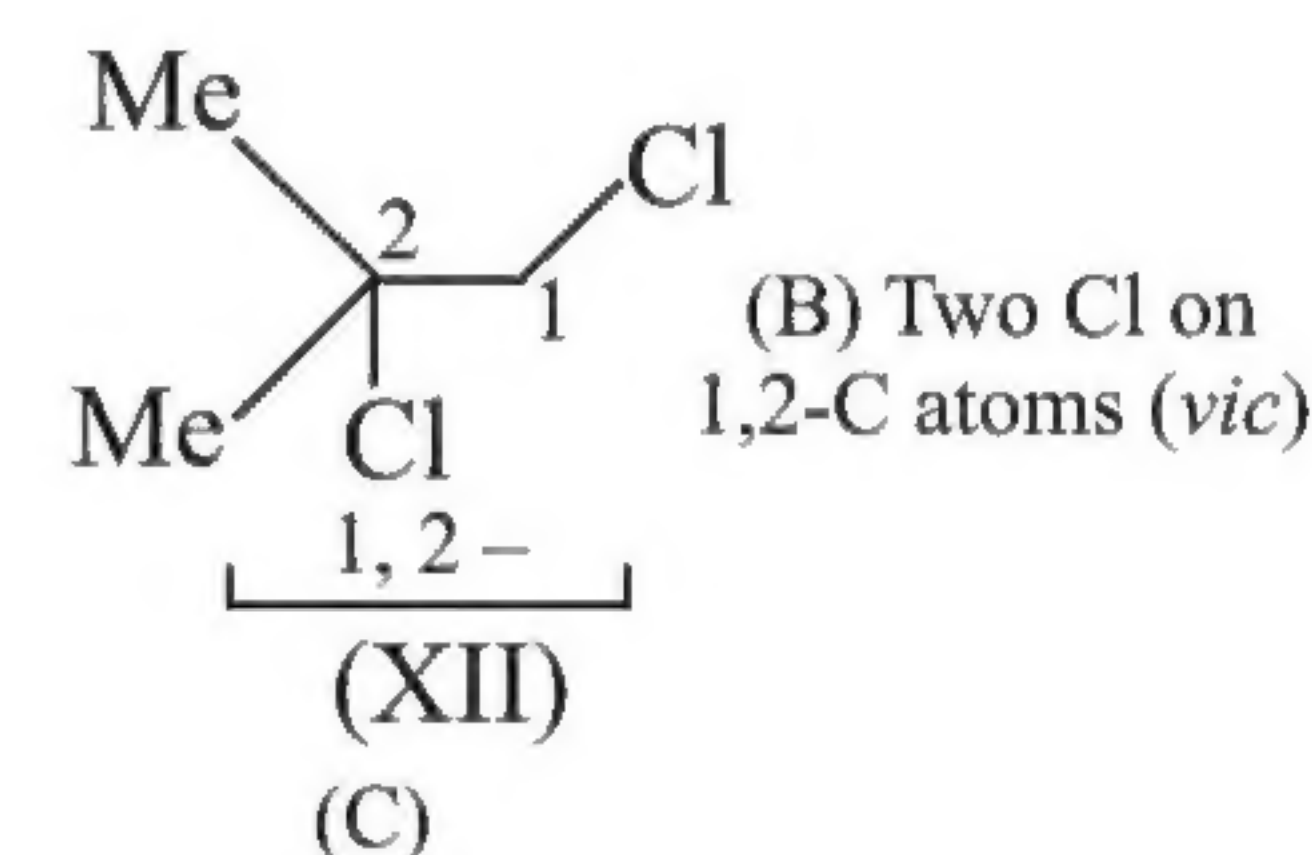
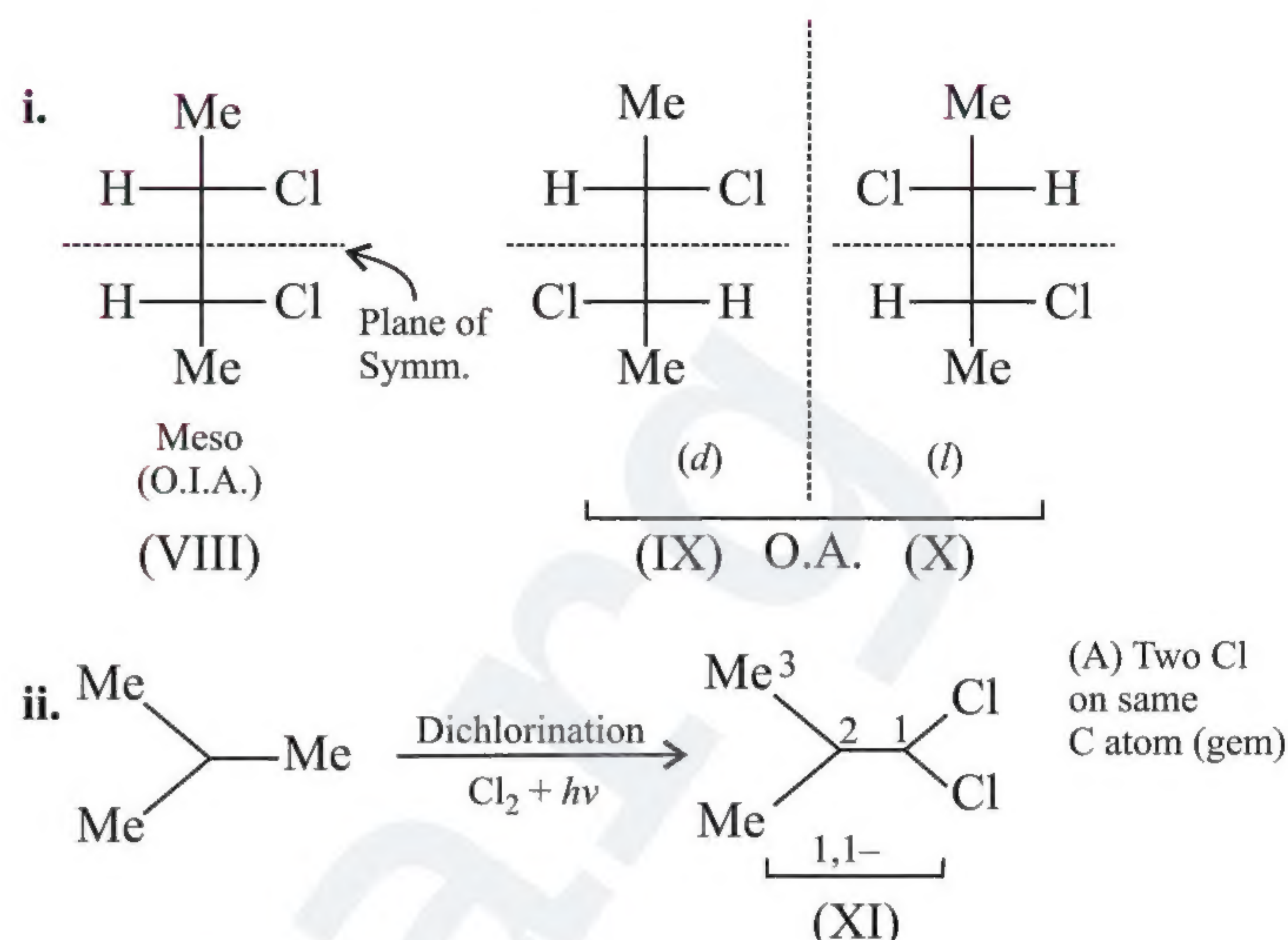
\therefore Value of $M = 11$ (Structural + Stereoisomers)

Value of $N = 8$ (Structural isomers)

b.



Structure of (VIII), (IX), (X) :

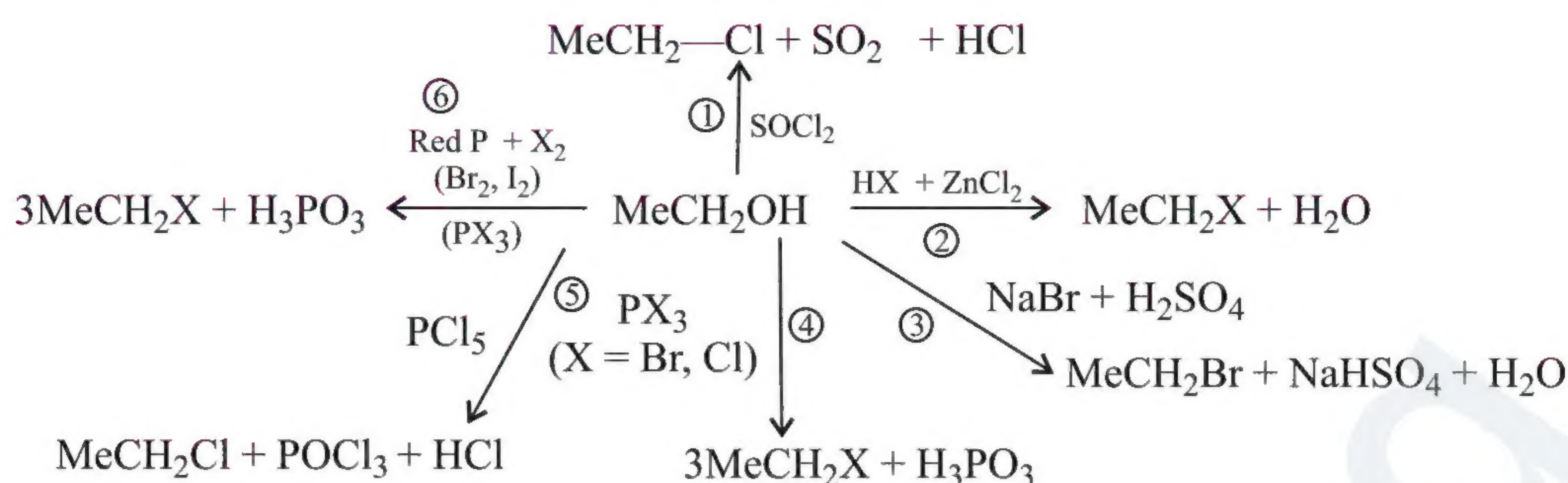


The value of $N = 13$ (Structural isomers = 9)

3.4 PREPARATION OF ALKYL HALIDES

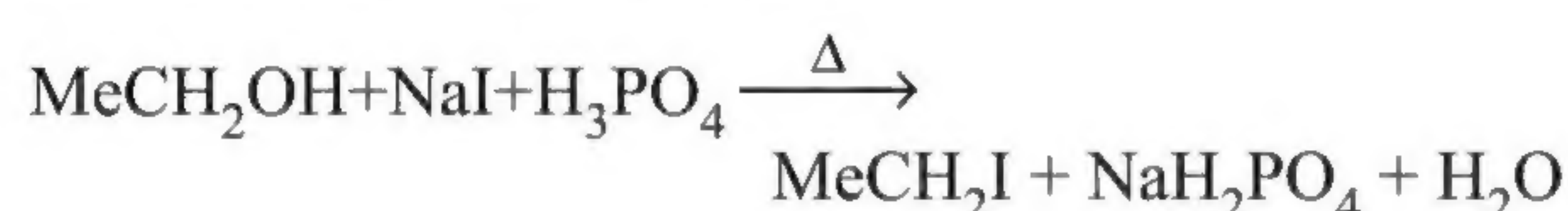
3.4.1 PREPARATION OF RX FROM ALCOHOLS

RX are best prepared from alcohols in which ($-\text{OH}$) group is replaced by halogens on reaction with concentrated HX (halogen acids), PX_3 (phosphorous halides), PCl_5 , or SOCl_2 (thionyl chloride). SOCl_2 is preferred because the byproducts (SO_2 and HCl) being gases easily escape leaving RCl in almost pure state. PBr_3 and PI_3 are unstable, so they are generated *in situ* (produced in the reaction mixture) by the reaction of red P_4 with Br_2 and I_2 , respectively. RCl is prepared from ROH by passing dry HCl or by heating ROH solution in concentrated aqueous HCl .



Note: In reactions (2) and (3) rearrangement occurs due to the formation of >C^{\oplus} ions.

- i. Alkyl iodides (RI) are prepared by ROH with NaI or KI in 95% H_3PO_4 . H_2SO_4 is not used, since it oxidises HI produced in the reaction to I_2 and thus prevents the reaction between ROH and HI to form RI; that is why non-oxidising acid H_3PO_4 is used.

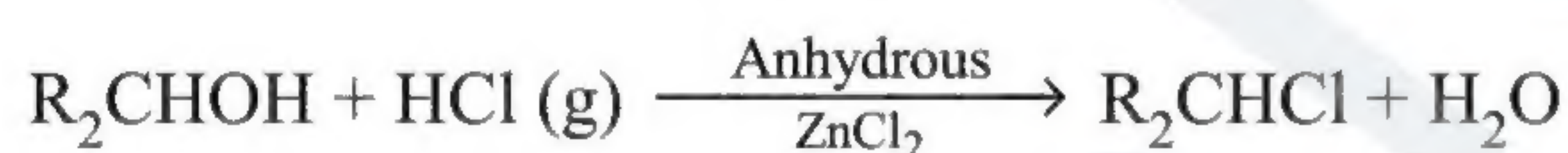
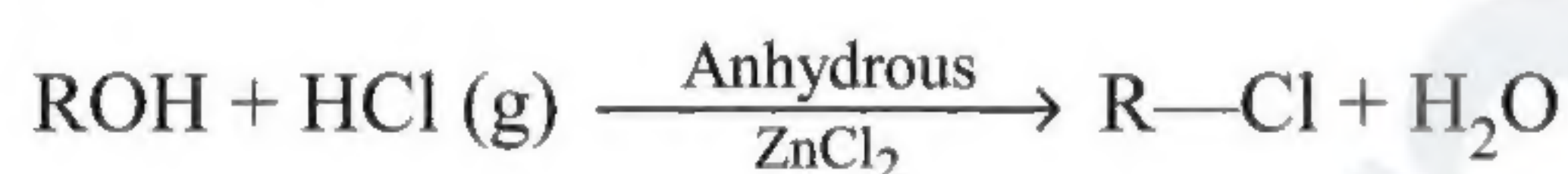


- ii. **Reactivity of alcohols:** $3^\circ > 2^\circ > 1^\circ$.

Reactivity of HX: $\text{HI} > \text{HBr} > \text{HCl}$

Since the reaction of ROH with HX is S_N reaction, the nucleophilic order of halide ions is: $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$ and order of stability of carbocation is $3^\circ \text{C}^{\oplus} > 2^\circ \text{C}^{\oplus} > 1^\circ \text{C}^{\oplus}$.

- iii. **Grove's process and Lucas test:**



This reaction is called **Grove's process**.

The purpose of ZnCl_2 is to help in the cleavage of (C—O) bond. Being a Lewis acid, it coordinates with the oxygen atom of the alcohols. As a result, (C—O) bond weakens and ultimately breaks to form carbocations. These carbocations then readily react with (Cl^-) ion to form chloroalkanes. Also, 3° alcohols react readily with conc. HCl even in the absence of ZnCl_2 .

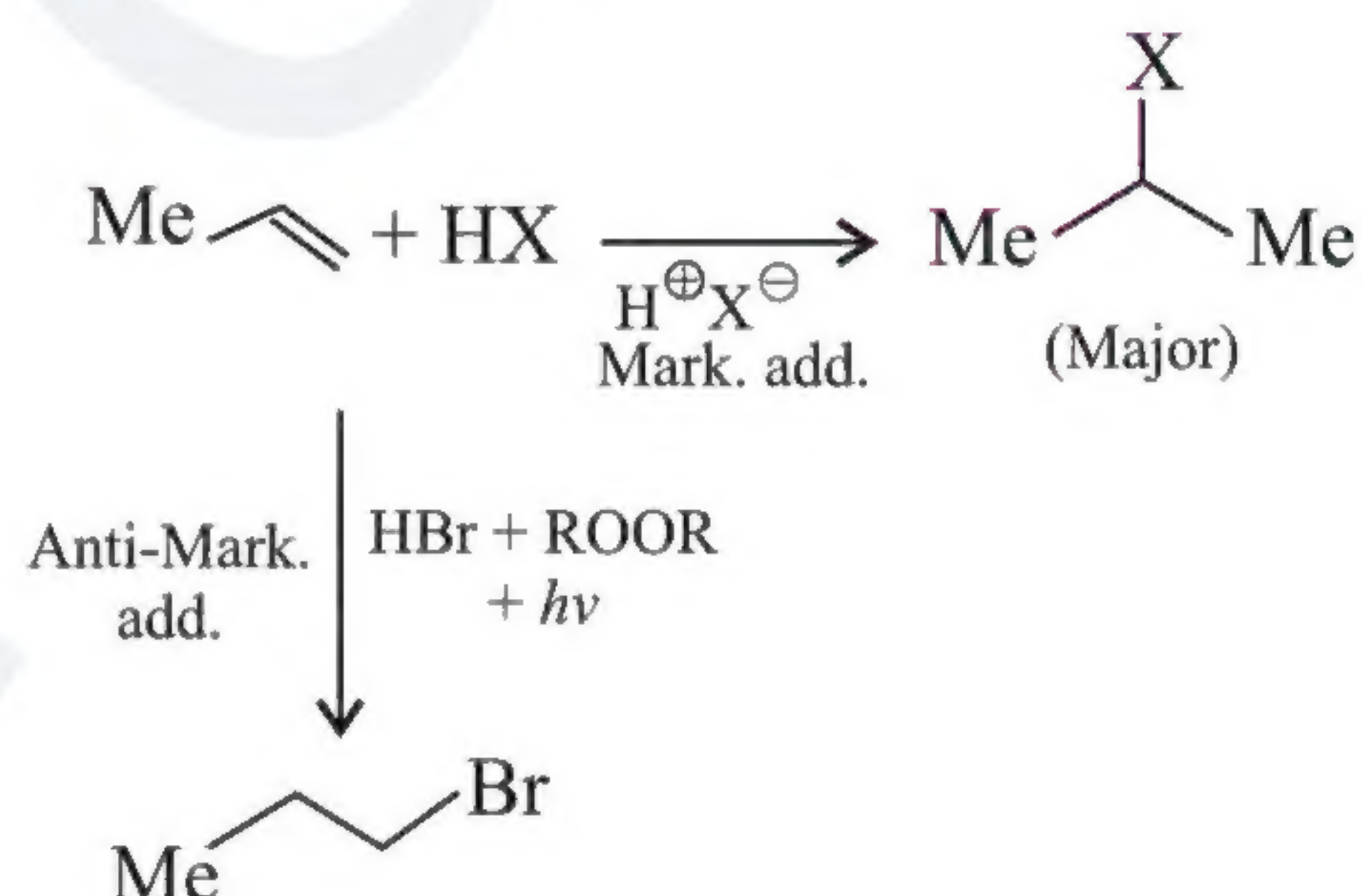
- iv. $\text{R}_3\text{C—OH} + \text{Conc. HCl} \xrightarrow{\text{Room temp.}} \text{R}_3\text{C—Cl} + \text{H}_2\text{O}$

This reaction is the basis of the **Lucas test**, which is used to distinguish between 1° , 2° , and 3° alcohols. Lucas reagent (conc. HCl + anhydrous ZnCl_2 : : 1 : 1) reacts with 3° alcohols. It gives white turbidity immediately due to the formation of insoluble alkyl chlorides and 2° alcohols give turbidity after five minutes, while 1° alcohols do not react with Lucas reagent at room temperature and hence no turbidity is formed. This can be explained by the stability of the carbonium ion ($3^\circ \text{C}^{\oplus} > 2^\circ \text{C}^{\oplus} > 1^\circ \text{C}^{\oplus}$).

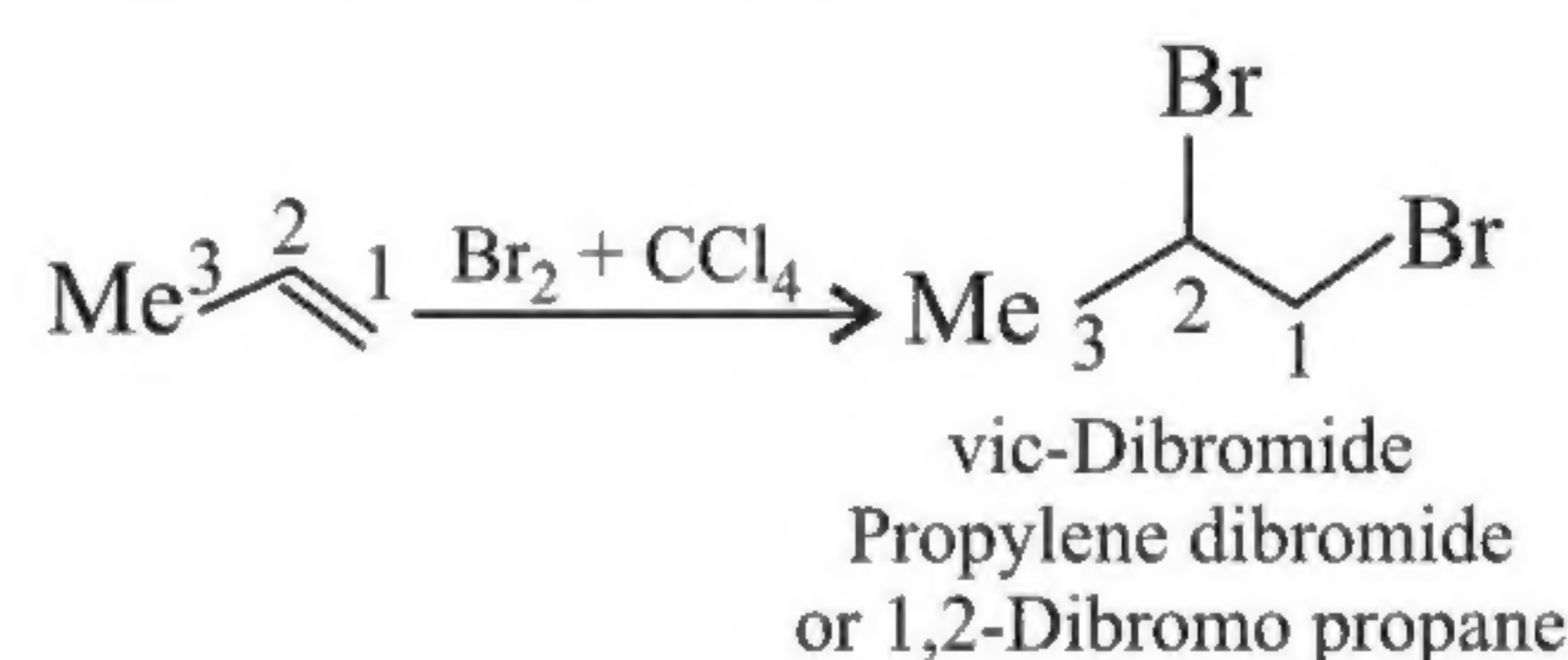
- v. ArX (aryl halides) cannot be prepared by the above method because the (C—O) bond in PhOH (phenols) has a partial double bond character due to resonance and is difficult to break as it is stronger than a single bond.

3.4.2 PREPARATION OF RX FROM ALKENES

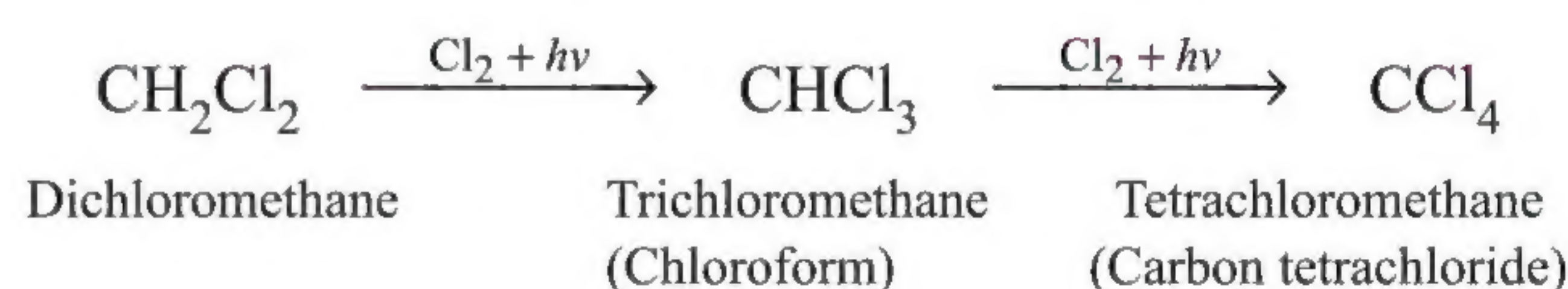
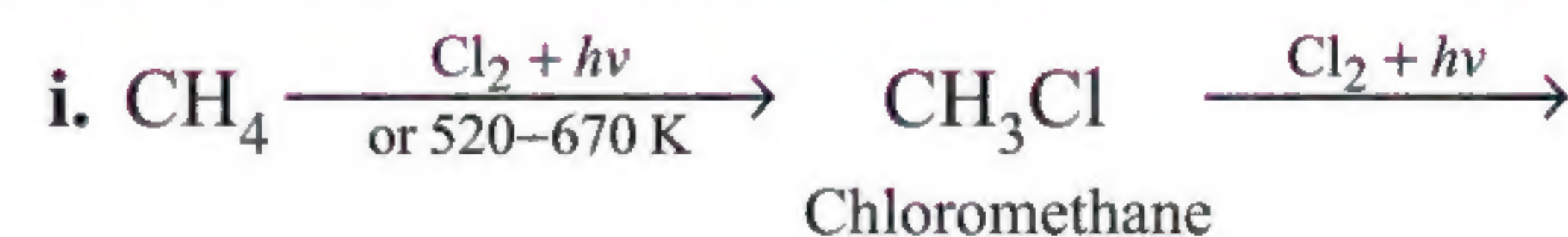
- i. **Addition of HX:**



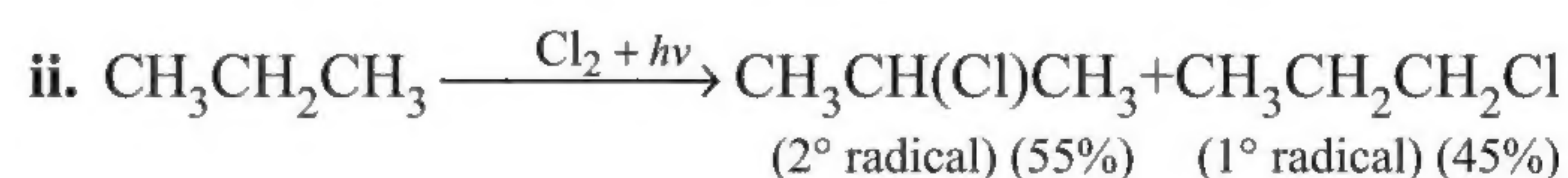
- ii. **Addition of halogen:**



3.4.3 HALOGENATION IN ALIPHATIC COMPOUNDS



This reaction takes place by free-radical substitution.



The relative amounts of these isomeric haloalkanes, however, depend upon the nature of halogen (Cl_2 or Br_2) and the number of types of hydrogens (1° , 2° , 3°) being substituted. Ease of substitution of various hydrogens is: $3^\circ > 2^\circ > 1^\circ$, but their relative rates vary with the nature of halogens. For example, with Cl_2 , the relative

rate of substitution of 3°, 2°, 1° hydrogens at 573 K is 5 : 3.8 : 1, while for Br₂ it is 1600 : 82 : 1.

Note: Bromination is selective and chlorination is reactive

3.4.4 HALOGEN EXCHANGE

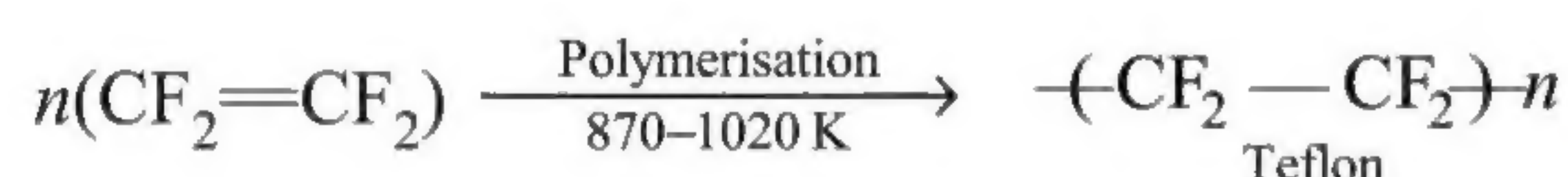
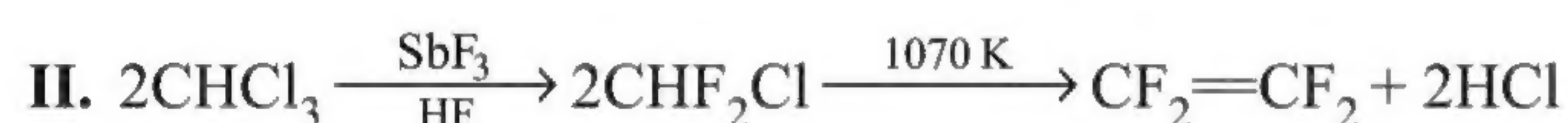
Iodination: Iodination of alkanes is generally not carried out to prepare alkyl iodides since the reaction is highly endothermic but carried out by **Finkelstein reaction**.

I[−] is better nucleophile & better leaving group.



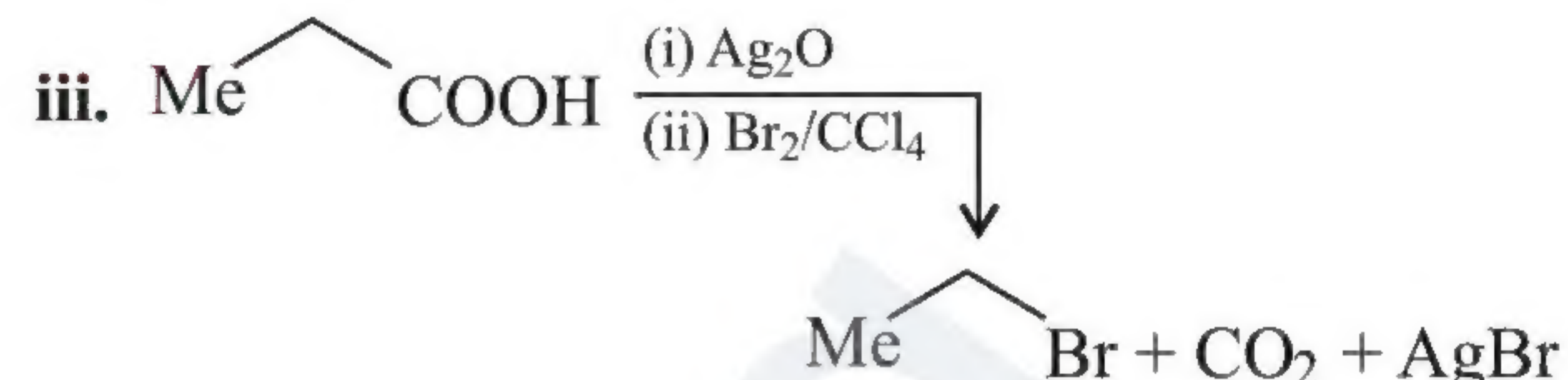
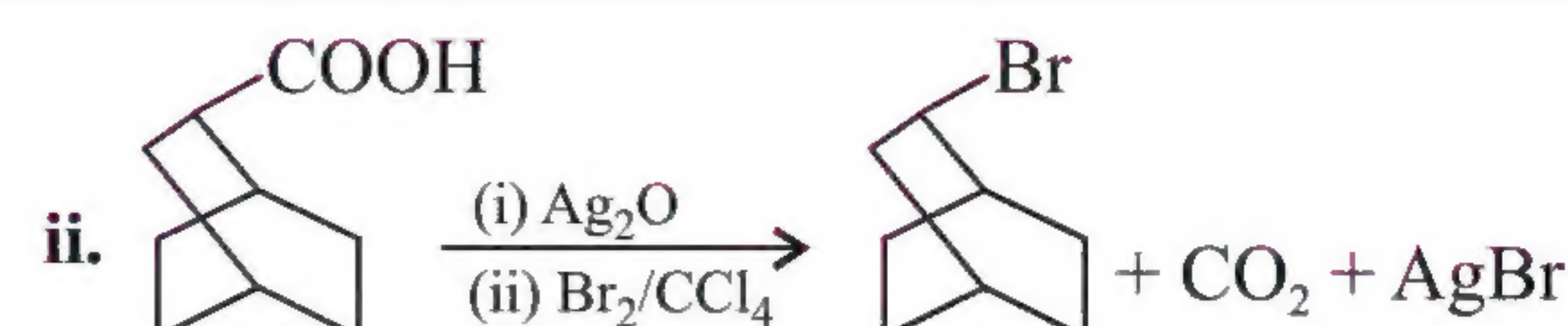
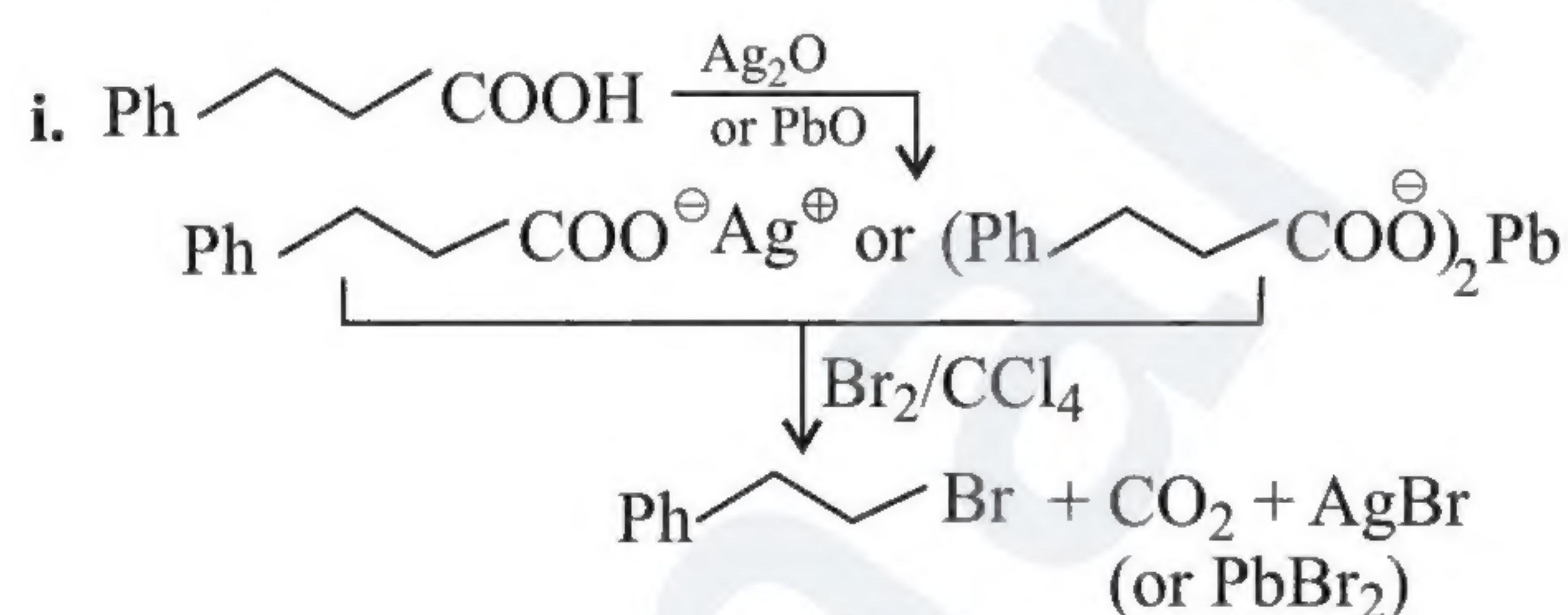
3.4.5 FLUORINATION (SWARTS REACTION)

Fluorination of alkanes takes place explosively with the rupture of (C—C) bond in higher alkanes. Therefore, alkylfluorides are usually prepared by heating haloalkanes with inorganic fluorides, such as AsF₃, SbF₃, AgF, Hg₂F₂, CoF₃, etc.



3.4.6 BORODINE–HUNSDIECKER AND BIRNBAUM–SIMONINI REACTIONS

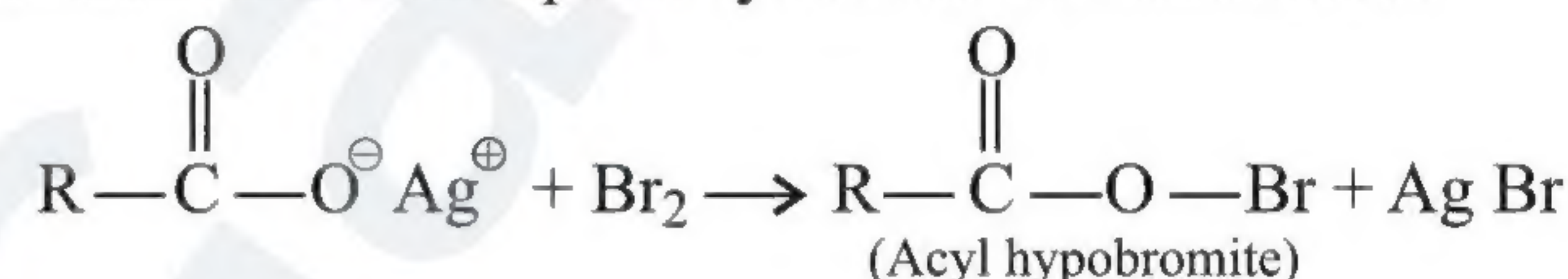
1. Bromoalkanes can be easily prepared by heating silver or lead salt of an acid with Br₂ in CCl₄. This brominative decarboxylation is called **Borodine–Hunsdiecker reaction**.



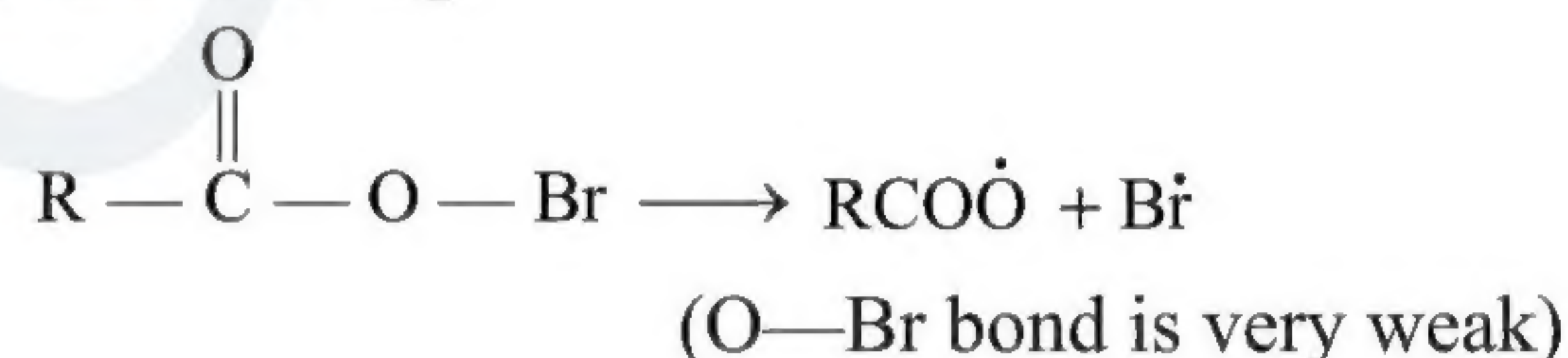
The yield of halide is 1° > 2° > 3°. Chloroalkanes can be prepared by using Cl₂. Iodoalkane cannot be prepared by this method. Iodine forms esters instead of (R—I) and is called **Birnbaum–Simonini reaction**.



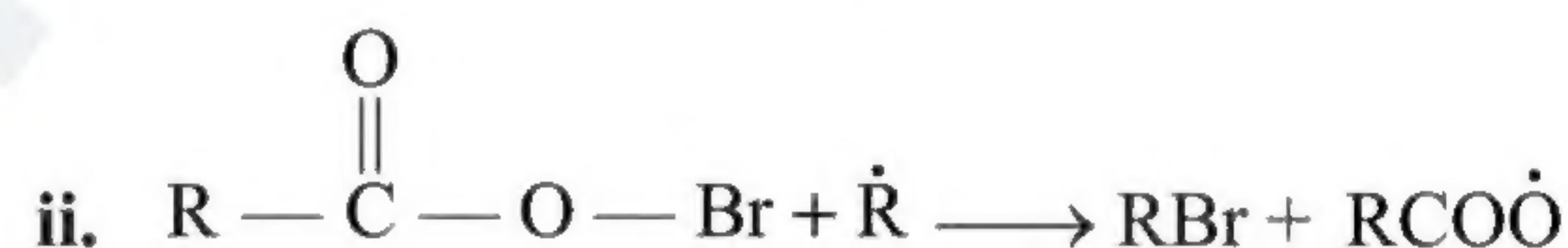
2. **Mechanism:** It takes place by free radical mechanism.



Chain initiation step:



Chain propagation step:

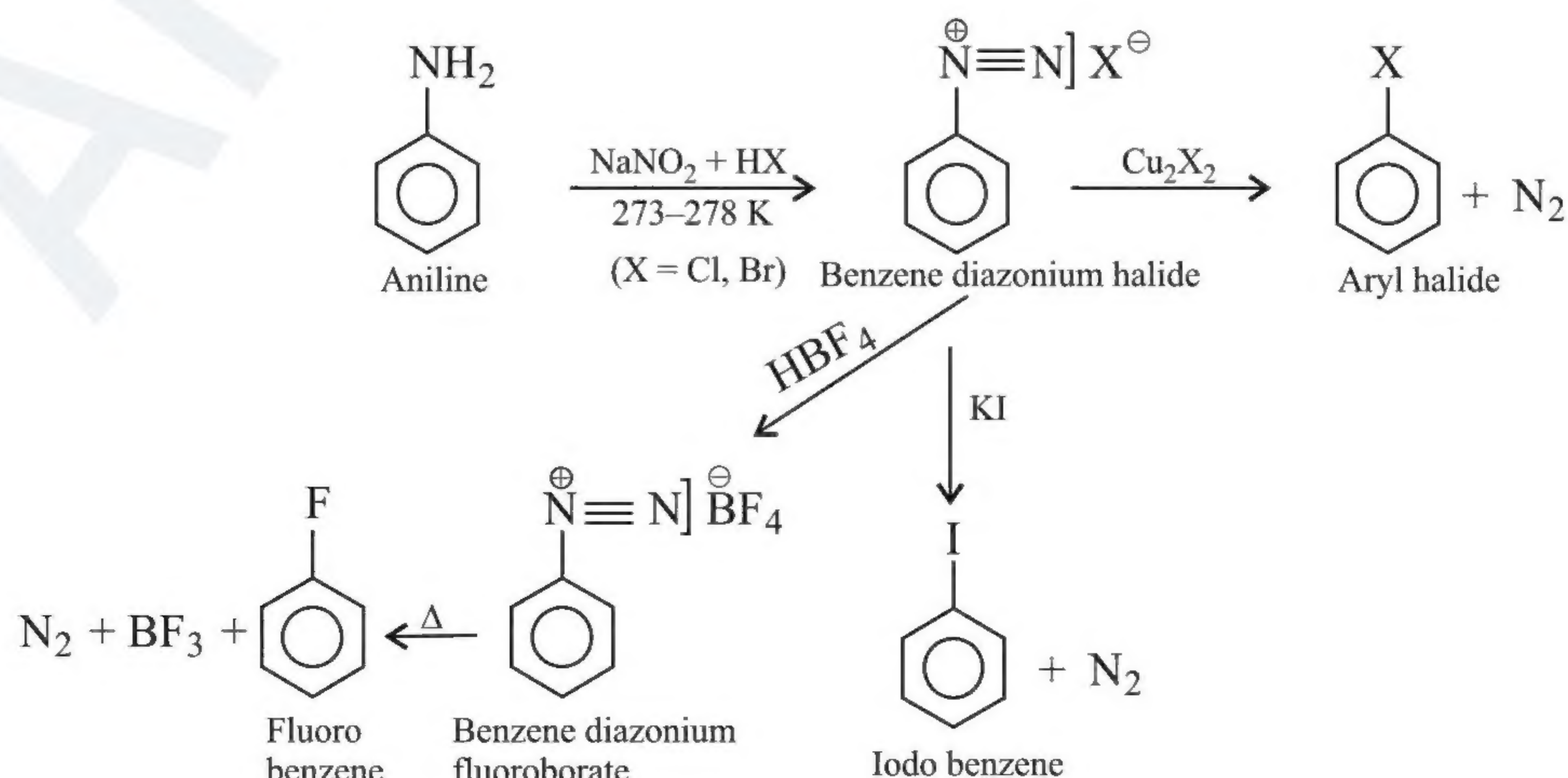


3.5 PREPARATION OF ARYL HALIDES

3.5.1 SANDMEYER'S REACTION

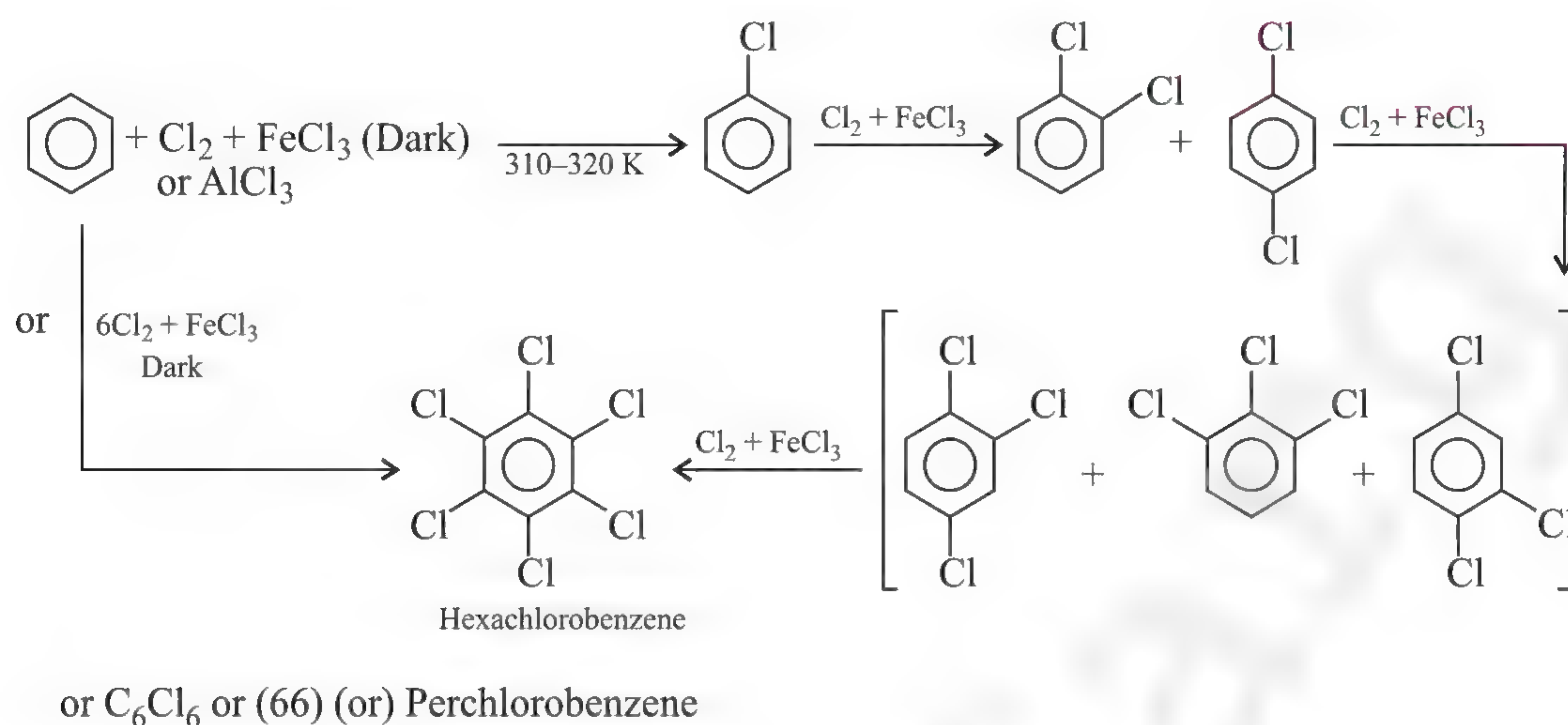
When diazonium salt is treated with Cu₂X₂ (cuprous chloride or bromide) at 273–278 K, the diazonium group is replaced by (—Cl) or (—Br) group to give ArCl or ArBr, whereas ArI and ArF are obtained by treating diazonium salt with KI and HBF₄ (fluoroboric acid), respectively.

Diazonium salts are prepared by the reaction of ArNH₂ with cold NaNO₂ and aqueous mineral acid.

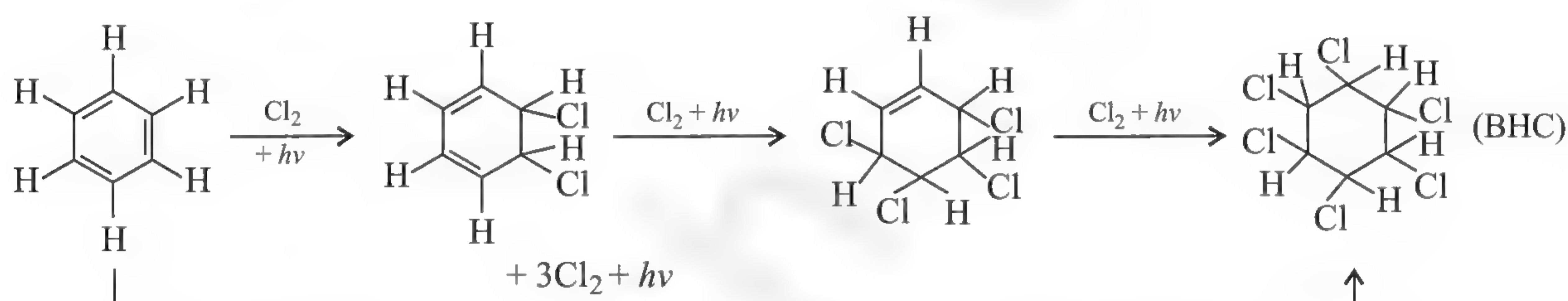


3.5.2 SE REACTION

i. **Halogenation:** (Catalytic halogenation, discussed earlier.) Electrophile is Cl^\oplus .

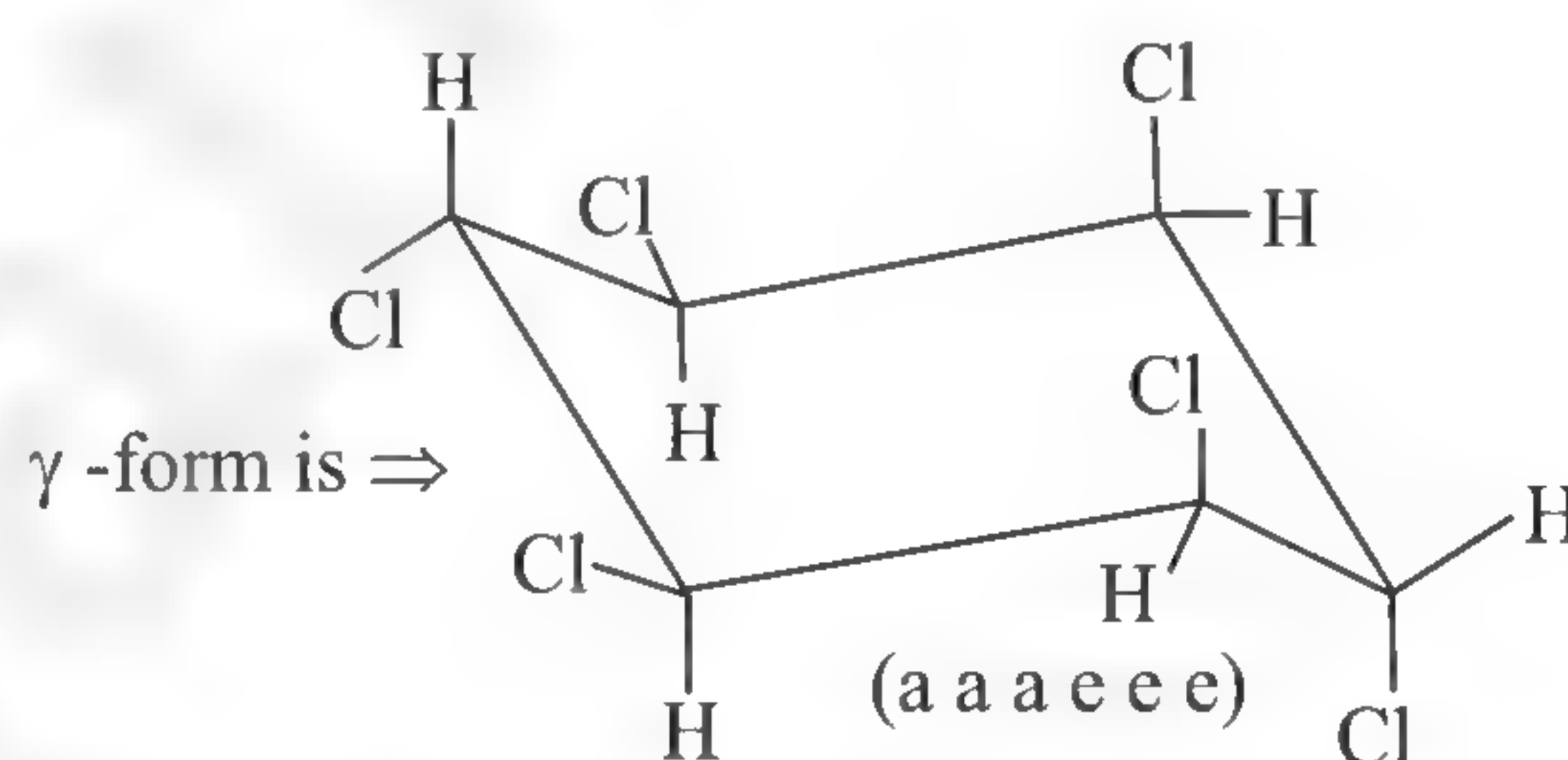


ii. Halogenation can be carried out in the presence of light. The reaction proceeds by free radical mechanism. This reaction is called free-radical addition reaction. ($\text{Cl}-\text{Cl} \xrightarrow{h\nu} 2 \text{Cl}^\bullet$)



B.H.C. \Rightarrow Benzene hexachloride (common name) and **IUPAC name is 1,2,3,4,5,6-hexachlorocyclo-hexane or $\text{C}_6\text{H}_6\text{Cl}_6$ or (666).**

B.H.C. is an insecticide or pesticide. It exists in eight geometrical isomers. Theoretically, seven are known: α , β , γ , δ , ϵ , η , θ . The γ -isomer is a powerful insecticide and is called Gammexane or Lindane or 666. It is extensively used as a pesticide in agriculture for exterminating (killing) termites (white ants) from soil.



All the isomers exist in the chair form and the conformations assigned for the various isomers are: (a = axial, e = equatorial)

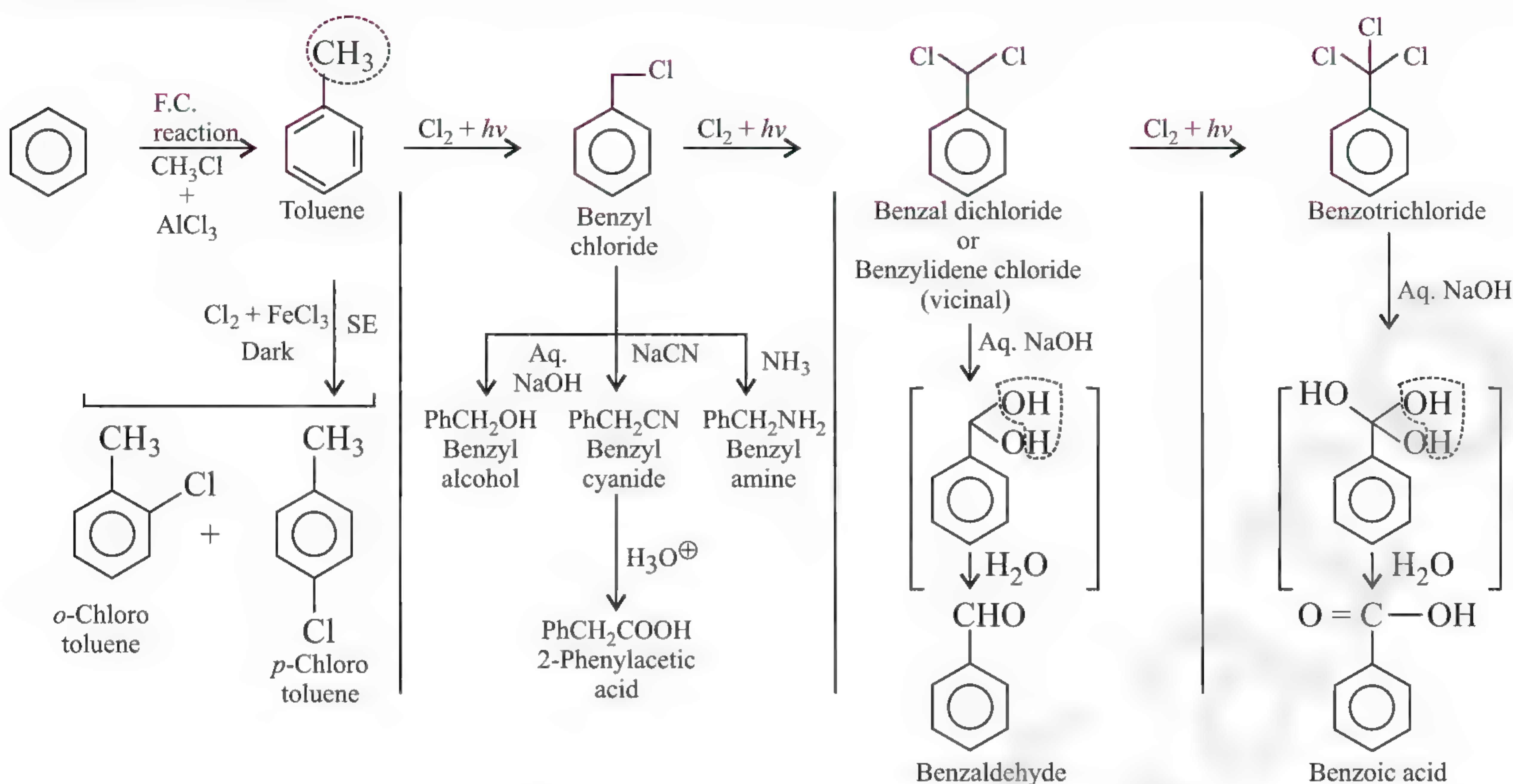
$\alpha \Rightarrow$ a a e e e e, $\beta \Rightarrow$ e e e e e e, $\gamma \Rightarrow$ a a a e e e,

$\delta \Rightarrow$ a e e e e e, $\epsilon \Rightarrow$ a e e a e e

Mullins (1955) suggested that the molecular size and shape are critical for the action of chlorinated hydrocarbon insecticides. According to Mullins, the molecule of γ -B.H.C. is smaller than those of other stereoisomers and hence can penetrate more readily.

3.5.3 SIDE-CHAIN HALOGENATION

Toluene with Cl_2 or Br_2 in the presence of light or at 600°C gives side-chain halogenation (allylic halogenation) products but with Lewis acid (FeCl_3 or FeBr_3) in dark, SE reaction occurs at *o*- and *p*-positions.



3.6 PHYSICAL PROPERTIES

a. Pure RX is colourless but RBr and RI develop colour when exposed to light and some of the volatile RX are sweet smelling.

b. **Melting and boiling points:** CH_3Br , CH_3Cl , $\text{C}_2\text{H}_5\text{Br}$, and some chlorofluoro methanes are gases at room temperature, whereas higher members are liquids or solids.

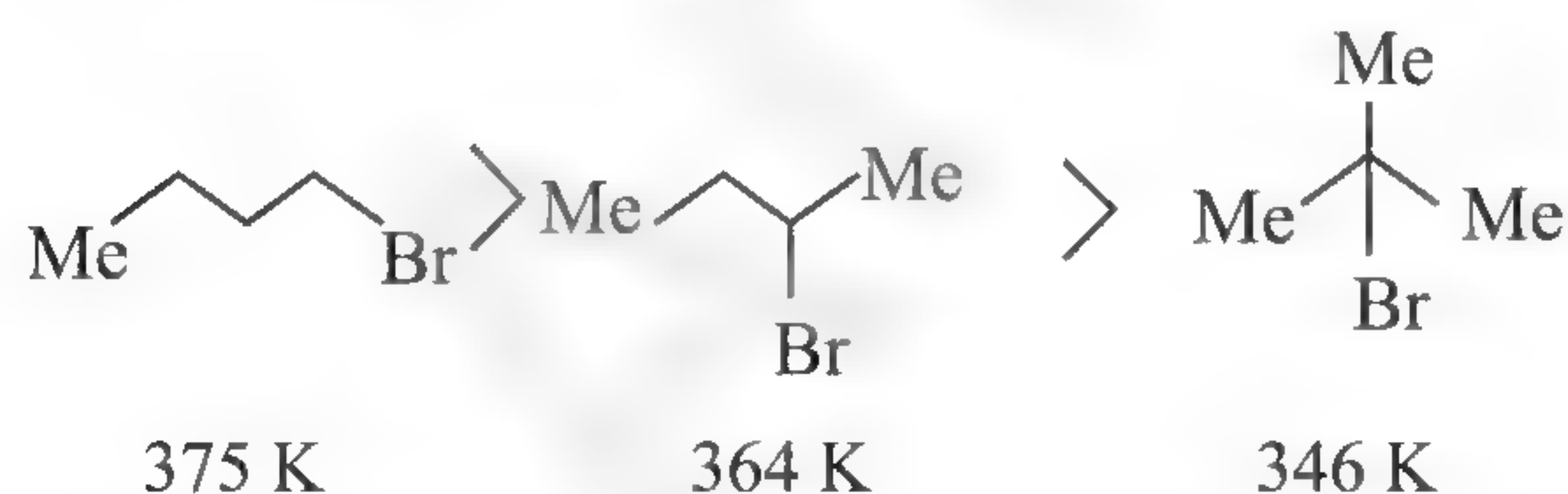
RX are polar, therefore intermolecular forces of attraction (e.g., dipole-dipole and van der Waals) are stronger in RX. Hence, the boiling point of RX is greater than those of hydrocarbons of comparable molecular masses.

The boiling point of $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$. Due to increase in size and mass of a halogen atom, the magnitude of van der Waals forces increases.

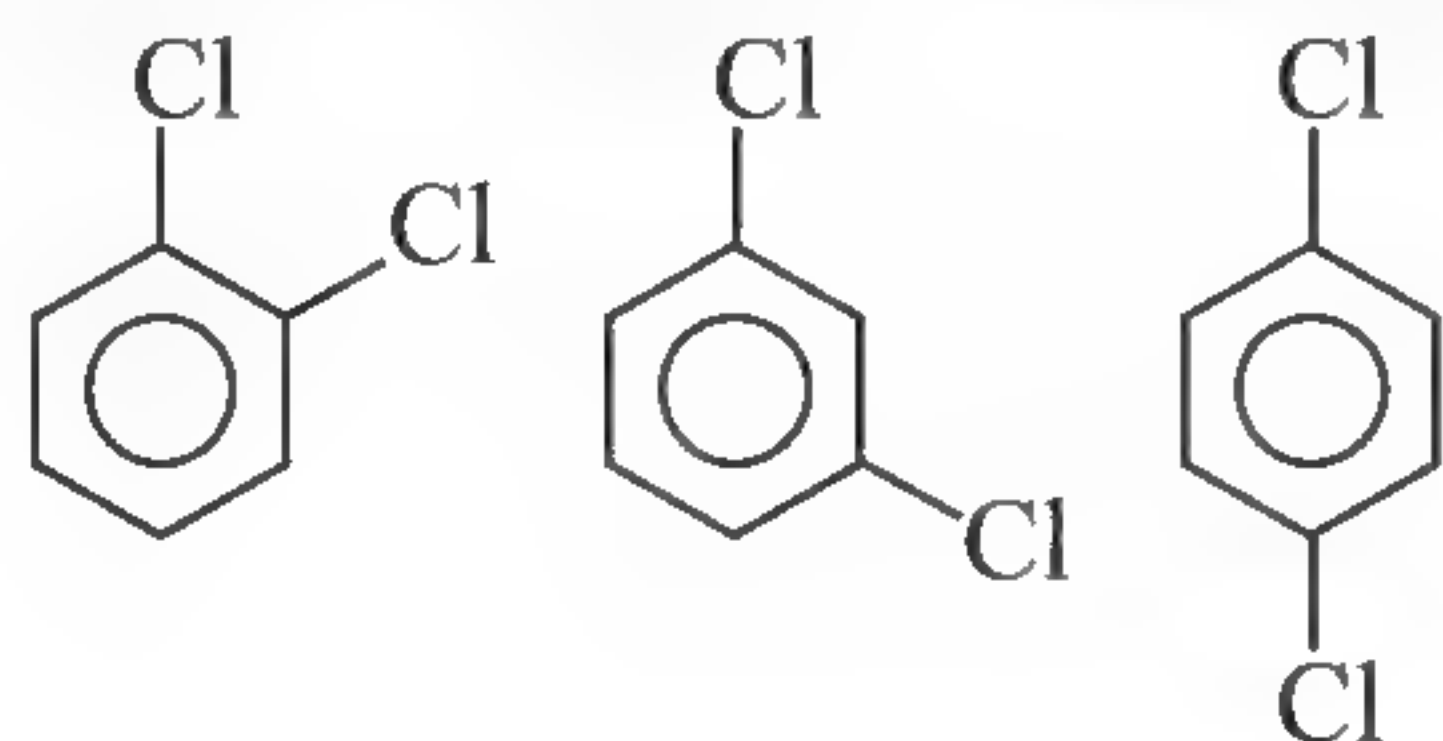
Branching decreases the surface area as in alkane because the branched C chains are more spherical-like, which results in lower boiling point.

Hence, the boiling point of isomeric RX decreases with increase in branching.

i. The boiling point of:



ii. The boiling point of dihalo benzene is nearly the same, but the melting point of *p*-isomer is higher than that of *o*- and *m*-isomers, due to symmetrical packing in its crystal lattice.



Melting point (K)	453	446	448
Boiling point	256	249	323

iii. Boiling point of (i) $\text{CCl}_4 > \text{HCCl}_3 > \text{H}_2\text{CCl}_2 > \text{H}_3\text{C-Cl}$
 350 334 313 251 K

Substituting Cl atoms on CH_4 increases the molecular mass and size causing the boiling point to increase. Hence, CCl_4 has the highest boiling point. Difference in boiling point becomes smaller as more Cl atoms are introduced due to increase in spherical nature of the molecule.

iv. Boiling point of $\text{C}_2\text{F}_6 > \text{C}_2\text{H}_6$.
 194 K 184 K

C_2F_6 (perfluoroethane) has a higher boiling point than C_2H_6 , due to its large molecular mass. But a small difference in the boiling point is due to F being only slightly larger than H and the low polarisability of F.

c. **Density:** The density of RX increases with the increase in the number of C atoms and X atoms, and the increase in atomic mass of X atoms.

i.

Compound:	$n\text{-C}_3\text{H}_7\text{I} > n\text{-C}_3\text{H}_7\text{Br} > n\text{-C}_3\text{H}_7\text{Cl}$				
Density (gm/ml)	1.75	1.33	0.89		
Compound:	$\text{CCl}_4 > \text{CHCl}_3 > \text{CH}_2\text{Cl}_2 > \text{H}_2\text{O} > \text{CH}_3\text{Cl}$				
Density (gm/ml)	1.59	1.48	1.34	1.0	0.92

ii. **Decreasing order of densities:**

$\text{RI} > \text{RBr} > \text{H}_2\text{O} > \text{RCl} > \text{RF} > \text{RH}$.

d. **Solubility:** RX and ArX are slightly soluble in H_2O and completely soluble in organic solvents (e.g., benzene, ether, and alcohols); although they are polar, they do not dissolve salts.

For the dissolution of RX or ArX in H_2O , energy is needed to overcome the attractive forces (dipole-dipole or van der Waals) between them and to break H-bonds between water molecules. Energy released is less when new attractions are formed between RX/ArX and H_2O molecules because they are

weaker than H-bonds in H_2O , which results in lower solubilities of RX/ArX in H_2O .

However, RX and ArX are soluble in organic solvents because the new intermolecular attractions between RX/ArX and organic solvent molecules are almost of the same strength as the forces of attraction being broken in separate RX/ArX and organic solvent molecules.

e. Stability:

Stability order is: $\text{R—F} > \text{R—Cl} > \text{R—Br} > \text{R—I}$

It is because of the bond strength order:

$\text{C—F} > \text{C—Cl} > \text{C—Br} > \text{C—I}$

Therefore, the RI is least stable and due to this reason RI in the presence of light decomposes to I_2 and becomes violet or brown.



f. Inflammability: RX or ArX are less inflammable than the corresponding hydrocarbons. With the increase of —X content, the inflammability decreases. Since they do not catch fire easily, they are widely used as solvents for fats and oils. CCl_4 is a good solvent for drycleaning.

3.7 S_N REACTIONS

Nucleophile reacts with substrate (R—X) having a positive charge on the C atom bonded to halogen, and the halide departs. Halide ion is called the leaving group.

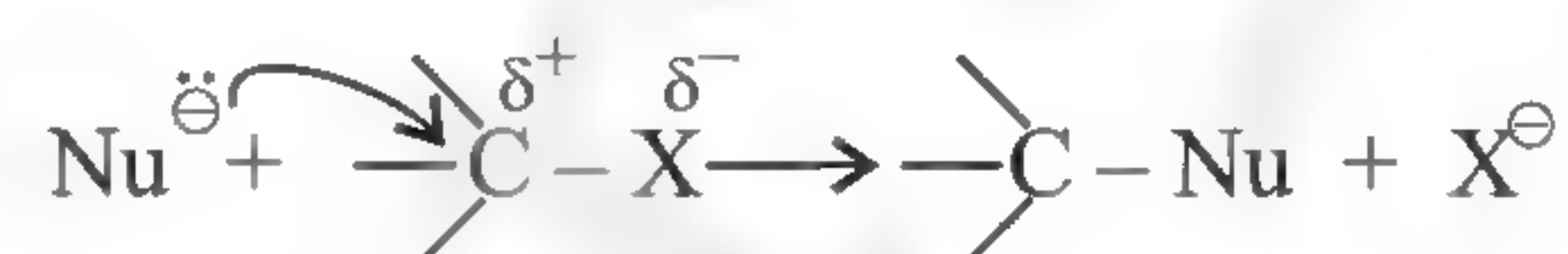
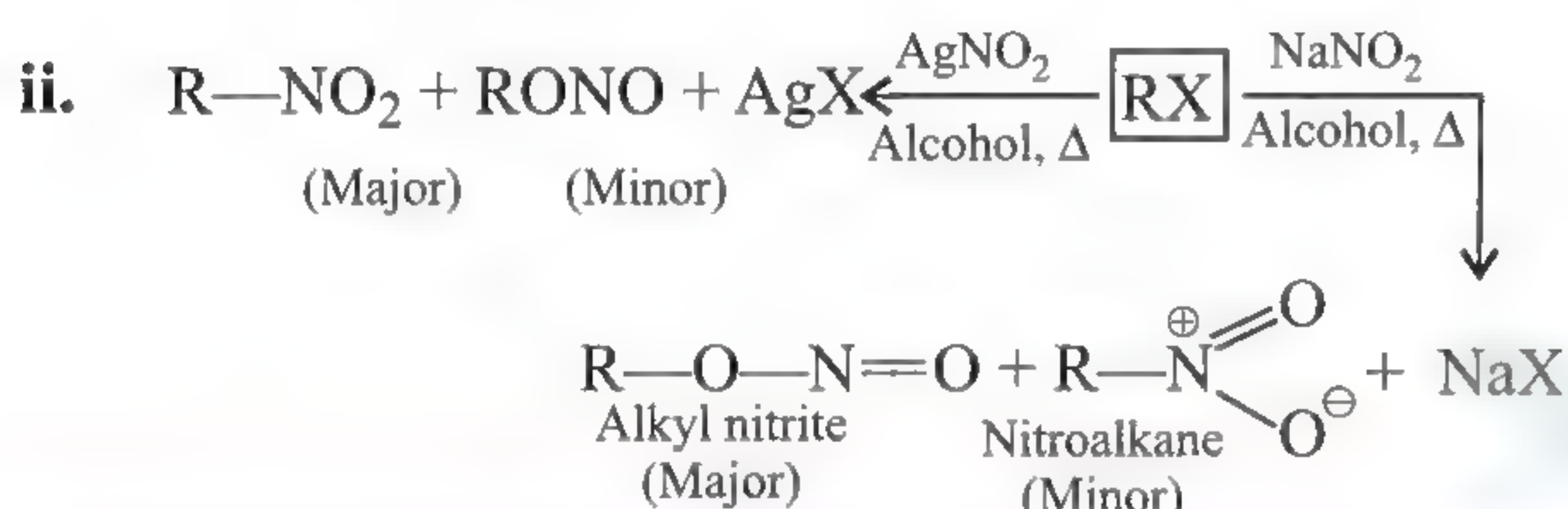
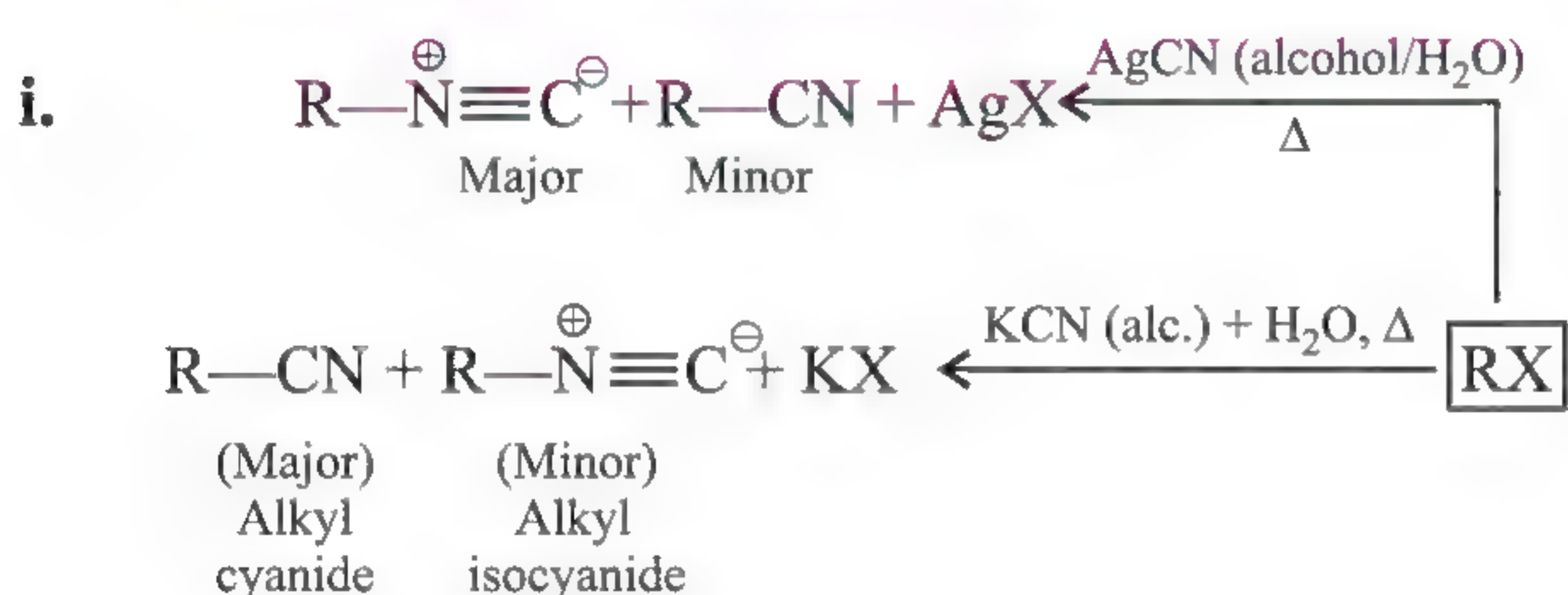


Table 3.3 The list of nucleophiles and the products formed by the reaction of (R—X) with nucleophile

S.No.	Reagent	Nucleophile Nu^\ominus	Reaction	Product	Class of product
1.	NaOH or KOH	OH^\ominus	$\text{OH}^\ominus + \text{R}-\text{X} \longrightarrow$	$\text{ROH} + \text{X}^\ominus$	Alcohol
2.	H_2O	H_2O	$\text{H}_2\text{O} + \text{R}-\text{X} \longrightarrow$	$\text{ROH} + \text{HX}$	Alcohol
3.	R'ONa or R'OK' (MeONa , EtONa $\text{Me}-\text{CH}_2-\text{ONa}$)	R'O^\ominus	$\text{R'O}^\ominus + \text{R}-\text{X} \longrightarrow$	$\text{ROR'} + \text{X}^\ominus$	Ether
4.	NaI or KI	I^\ominus	$\text{I}^\ominus + \text{R}-\text{X} \longrightarrow$	$\text{RI} + \text{X}^\ominus$	Alkyl iodide
5.	NH_3	NH_3	$\text{NH}_3 + \text{R}-\text{X} \longrightarrow$	$\text{RNH}_2 + \text{HX}$	1° amine
6.	R'NH_2	R'NH_2	$\text{R'NH}_2 + \text{R}-\text{X} \longrightarrow$	$\text{R-NHR'} + \text{HX}$	2° amine
7.	R'R''NH	R'R''NH	$\text{R'R''NH} + \text{R}-\text{X} \longrightarrow$	$\text{R}-\text{N}(\text{R'')}-\text{R'} + \text{HX}$	3° amine
8.	KCN or NaCN	$\text{C}\equiv\text{N}^\ominus$ or Cs CN	$\text{C}\equiv\text{N}^\ominus + \text{R}-\text{X} \longrightarrow$	$\text{R}-\text{C}\equiv\text{N} + \text{X}^\ominus$	Cyanide (Nitrile)
9.	$\text{Ag}-\text{C}\equiv\text{N}$	$\text{Ag}-\text{C}\equiv\text{N}$	$\text{Ag}-\text{C}\equiv\text{N} + \text{R}-\text{X} \longrightarrow$	$\text{R}-\text{N}^+\equiv\text{C}^\ominus + \text{X}^\ominus$	Isocyanide (Isonitrile)
10.	NaNO_2 or KNO_2	$\text{O}=\text{N}-\text{O}^\ominus$	$\text{O}=\text{N}-\text{O}^\ominus + \text{R}-\text{X} \longrightarrow$	$\text{R}-\text{O}-\text{N}=\text{O} + \text{X}^\ominus$	Alkyl nitrite
11.	AgNO_2	$\text{Ag}-\text{O}-\text{N}=\text{O}$	$\text{Ag}-\text{O}-\text{N}=\text{O} + \text{R}-\text{X} \longrightarrow$	$\text{R}-\text{N}(\text{O})_2 + \text{X}^\ominus$	Nitroalkane

12.	R'COOAg	$\text{R}'-\text{C}(=\text{O})-\text{O}^\ominus$	$\text{R}'-\text{C}(=\text{O})-\text{O}^\ominus \curvearrowright \text{R}-\text{X}$	$\text{R}'-\text{C}(=\text{O})-\text{O}-\text{R} + \text{X}^\ominus$	Ester
13.	LiAlH ₄ or NaBH ₄ or NaAlH ₄	H [⊖]	H [⊖] \curvearrowright R-X	RH + X [⊖]	Alkane
14.	$\overset{\delta+\delta}{\text{RLi}}$ or $\overset{-\delta}{\text{R}}\overset{+\delta}{\text{MgX}}$	R [⊖]	R [⊖] \curvearrowright R-X	R-R + X [⊖]	Alkane
15.	R—C≡CNa	R—C≡C [⊖]	R—C≡C [⊖] \curvearrowright R-X	R—C≡C—R + X [⊖]	Alkyne
16.	NaSH	SH [⊖]	HS [⊖] \curvearrowright R-X	R—SH + X [⊖]	Thiols (Mercaptans)

3.7.1 FORMATION OF CYANIDES, ISOCYANIDES, NITRO, AND NITRITES

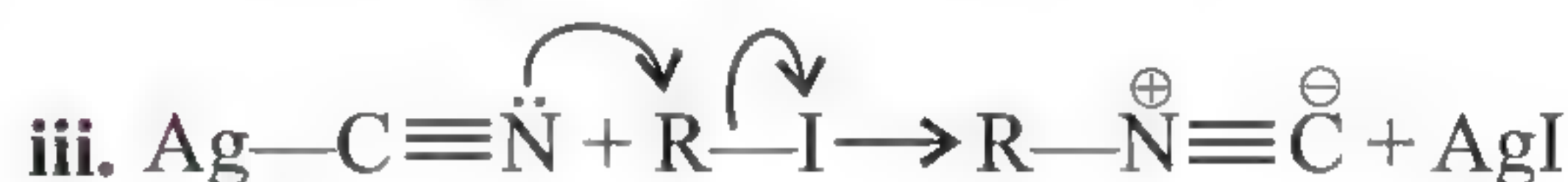
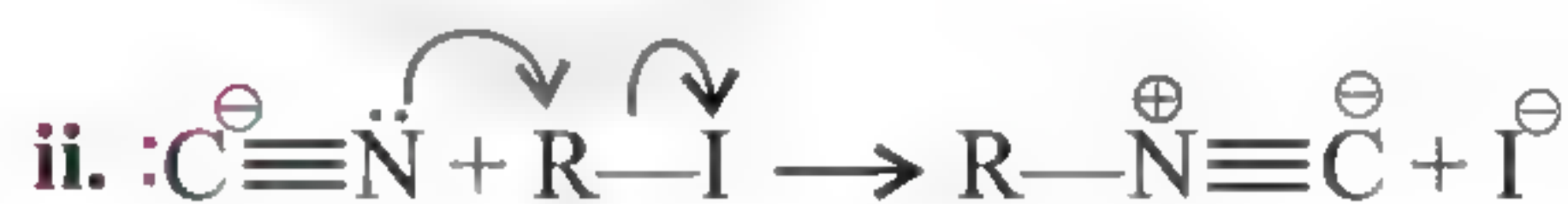
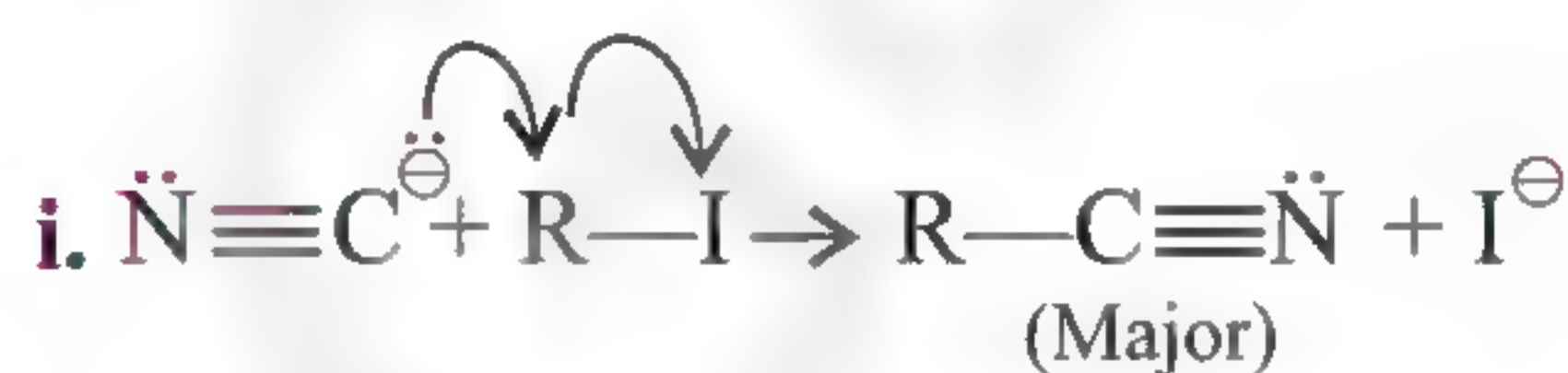


Note: Aryl cyanides and aromatic nitro compounds cannot be prepared by this method since aryl halides are most unreactive towards nucleophilic substitution reaction (S_N).

(a) Explanation:

This is an example of S_N reaction in which CN^\ominus ions act as nucleophiles, called an **ambident nucleophile**, in which both C and N atoms have a pair of \bar{e} 's and hence either C or N atom acts as the \bar{e} donor to the alkyl group. (CN^\ominus) group is a hybrid of two resonance-contributing structures ($:\text{C}^\ominus\equiv\text{N} \leftrightarrow :\text{C}\equiv\text{N}^\ominus$). Alkali metal cyanides are predominantly ionic to give CN^\ominus ion. The reaction can occur through either C or N and can give both cyanides and isocyanides. But the reaction occurs through carbon since (C—C) bonds are stronger than (C—N) bonds and hence alkyl cyanides are the chief products.

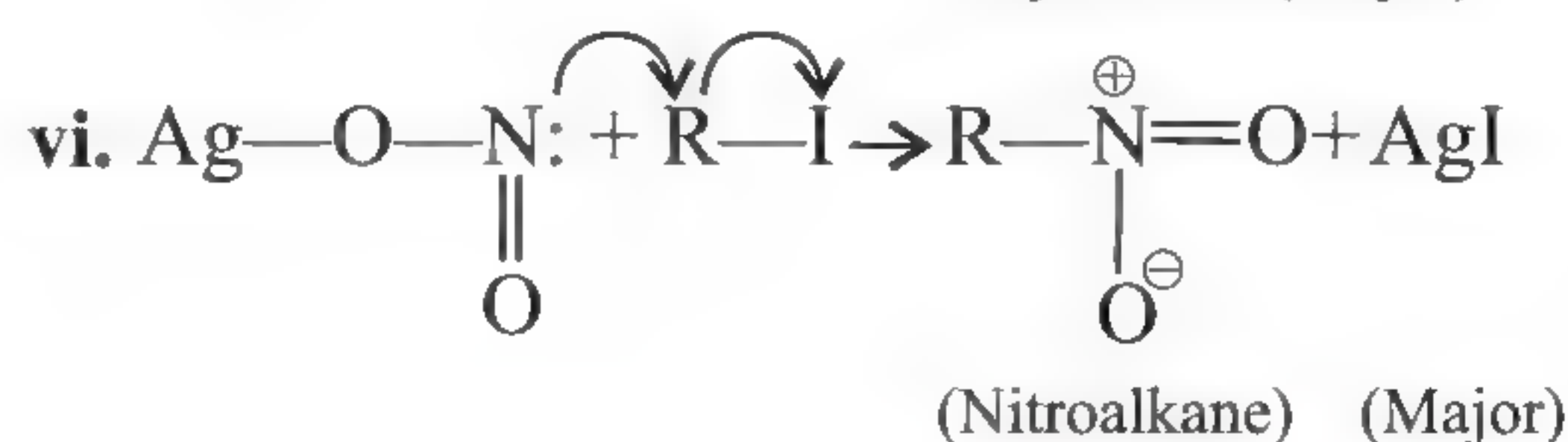
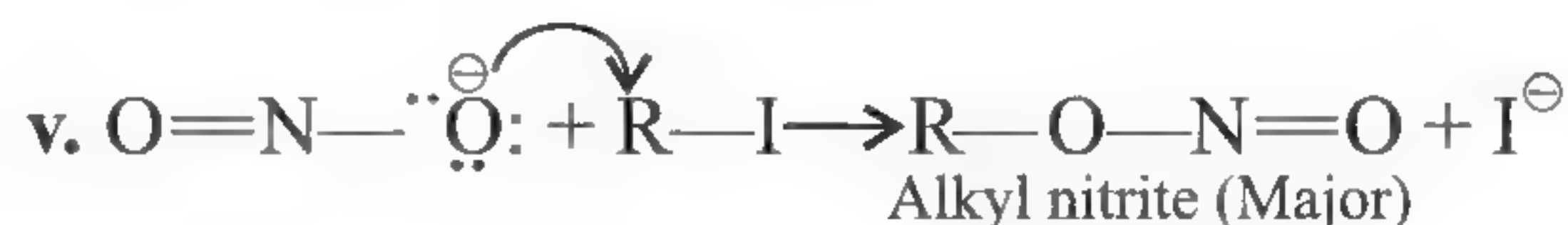
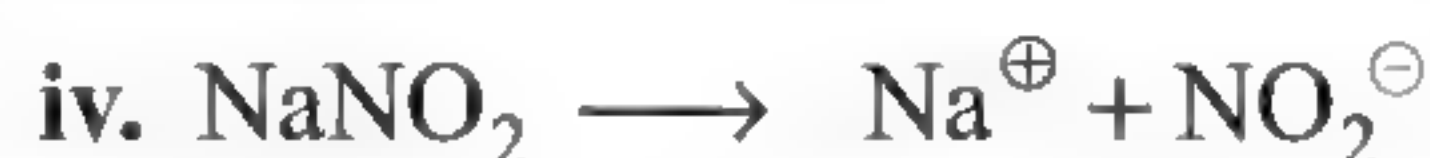
On the other hand, silver cyanide is predominantly covalent. Consequently, only nitrogen \bar{e} pair is available for bond formation. As a result, alkyl isocyanides are the chief products. Silver cyanide shows very small amount of ionic character, which also explains the formation of alkyl cyanide in small amount.



Similarly, the formation of nitro and nitrite compounds can be explained since NO_2^\ominus ion also exists as an ambident nucleophile with two different points of linkage $[\text{:}\ddot{\text{O}}^\ominus-\ddot{\text{N}}=\ddot{\text{O}}:]$. The linkage through oxygen results in alkyl nitrites, while through nitrogen atom it leads to nitroalkanes.

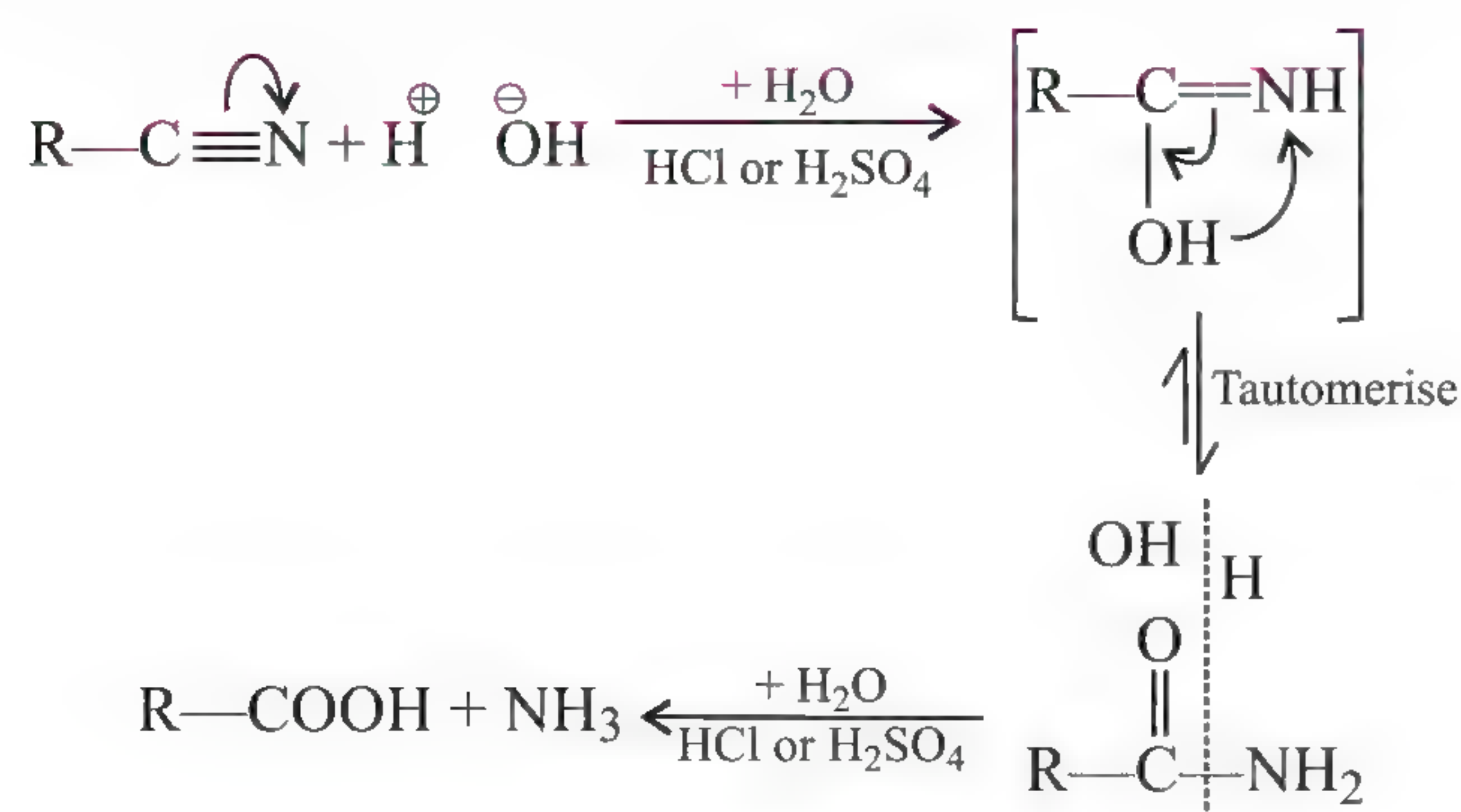
Alkali metal nitrites are predominantly ionic to give NO_2^\ominus ion. The reaction can occur through either O or N, which can give both nitrites and nitro compounds. But since (C—O) bonds are stronger than (C—N) bonds, alkyl nitrites are the chief products.

On the other hand, silver nitrite is predominantly covalent. Consequently, only nitrogen \bar{e} pair is available for bond formation. As a result, nitroalkanes are the chief products. Silver nitrite shows small amount of ionic character, which also explains the formation of alkyl nitrite in small amount.



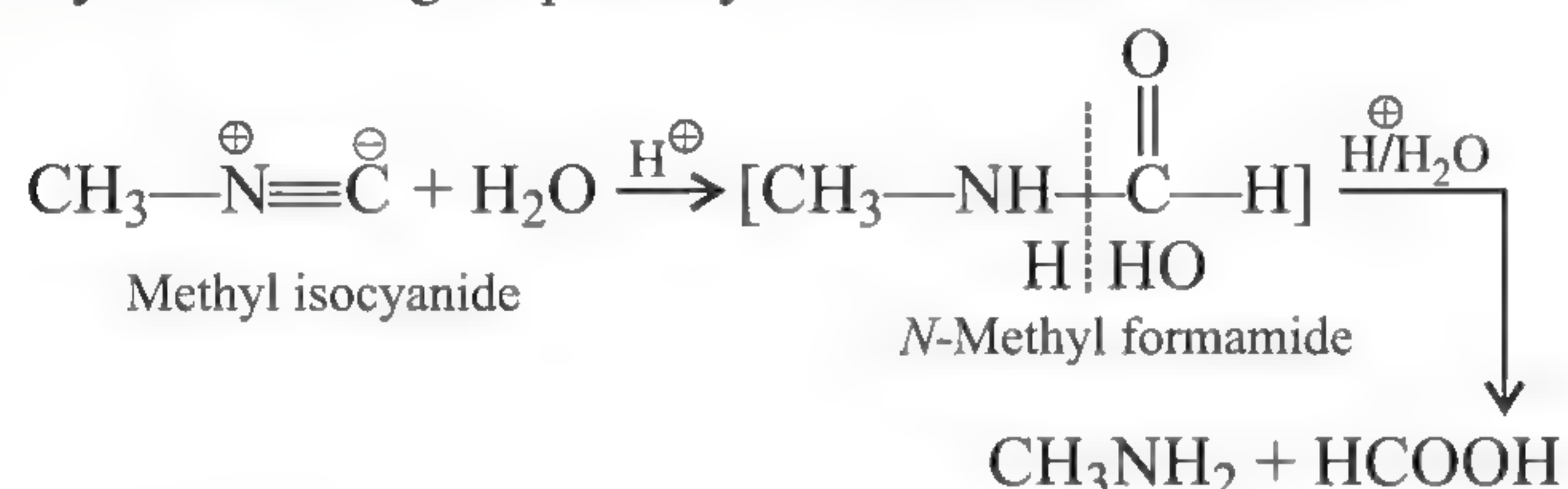
3.7.2 HYDROLYSIS OF (R—C≡N)

Hydrolysis of cyanides on boiling with an aq. mineral acid or alkali gives corresponding amides, which finally give acids and ammonia.

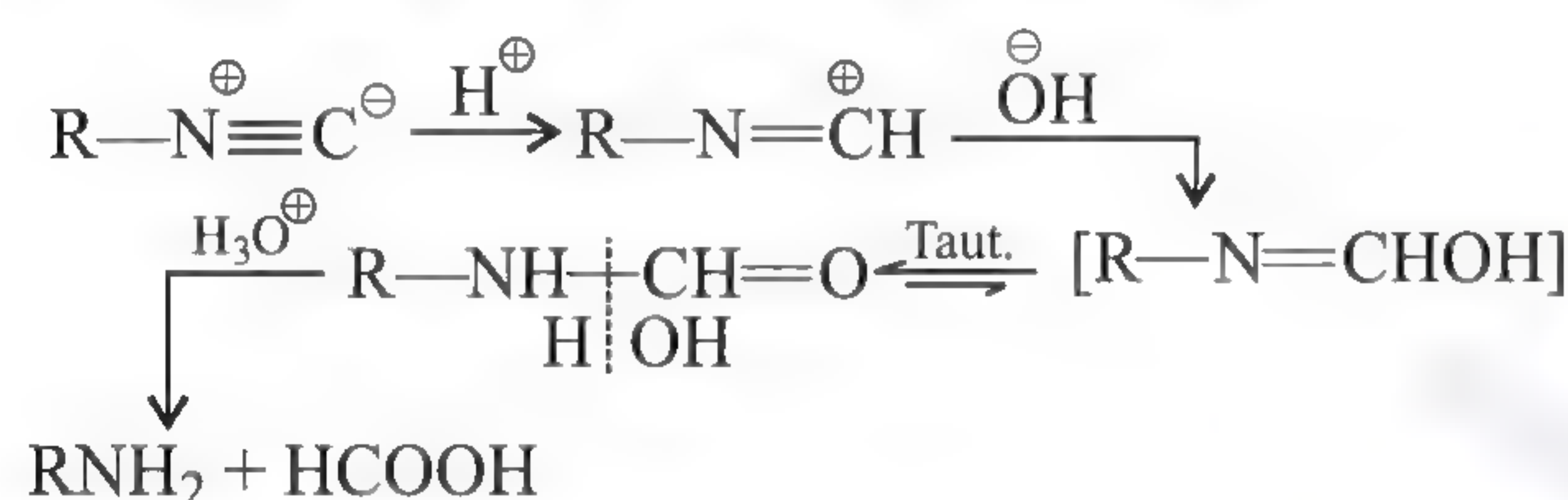


3.7.3 HYDROLYSIS OF (R—N≡C)

Isocyanides, on the other hand, are hydrolysed by dilute acids but not by alkalis to give primary amines and formic acid.



First, E^+ adds to the C and then Nu^- adds to the same C.



Explanation: The negative charge present on the C atom in isocyanides initially attracts electrophile (i.e., H^+) but repels nucleophile (OH^-). As a result, isocyanides are hydrolysed only by acids but not by alkalis. Once a proton gets attached to the negatively charged C atom, the tendency of this C atom to attract a nucleophile increases due to the presence of a positive charge on the N atom and thus facilitates hydrolysis as shown below:

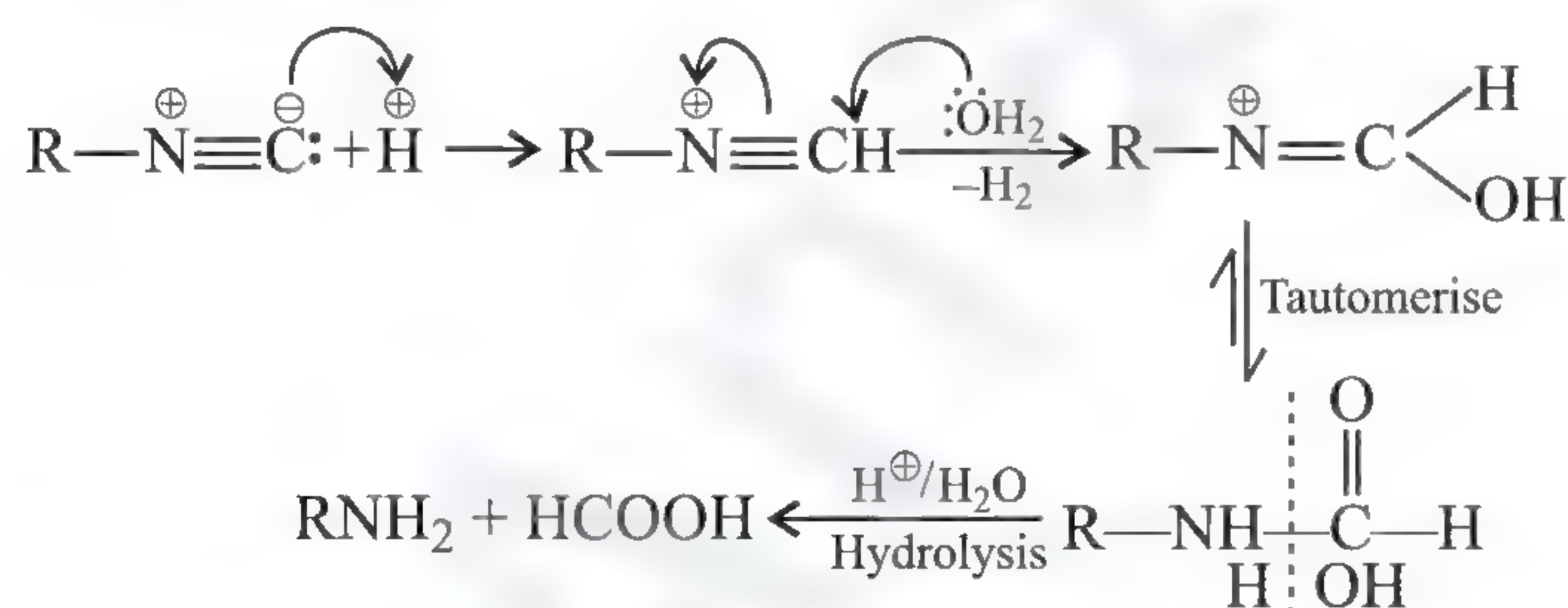


ILLUSTRATION 3.5

Haloalkanes react with KCN to form alkyl cyanides as main product while AgCN forms isocyanides as the chief product. Explain.

Sol. KCN is predominantly ionic and provides cyanide ions in solution. Although both carbon and nitrogen atoms are in a position to donate electron pairs, the attack takes place mainly through carbon atom and not through nitrogen atom since C—C

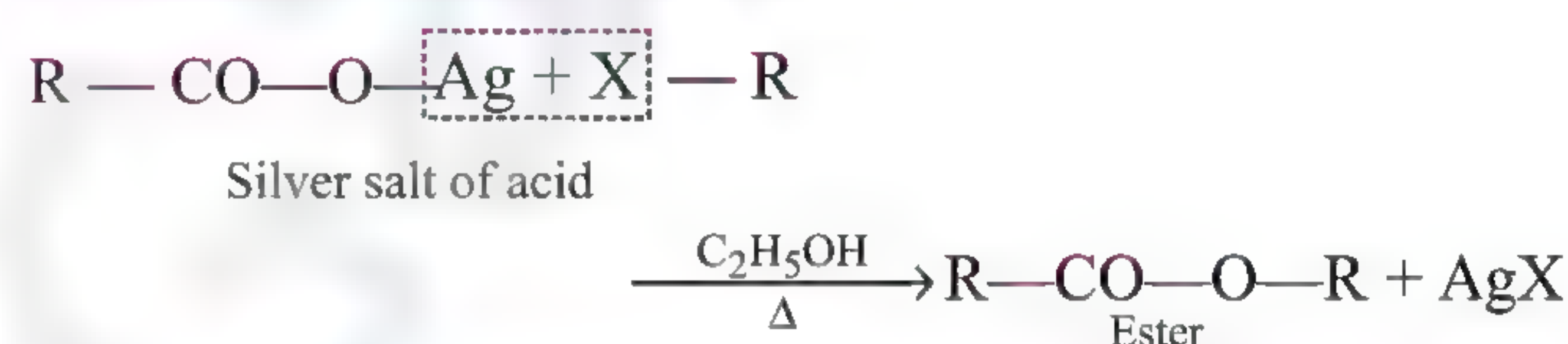
bond is more stable than C—N bond. However, AgCN is mainly covalent in nature and nitrogen is free to donate electron pair forming isocyanide as the main product.

3.8 FORMATION OF ALCOHOLS, ETHERS, ESTERS, AMINES, THIOALCOHOLS, THIOETHERS, ETC.

3.8.1 FORMATION OF ALCOHOLS

- $\text{RX} + \text{KOH (Aq.)} \longrightarrow \text{ROH} + \text{KX}$
- $\text{RX} + \text{AgOH (or moist silver oxide)} \longrightarrow \text{ROH} + \text{AgX}$

3.8.2 FORMATION OF ESTERS



3.8.3 HOFMANN AMMONOLYSIS OF ALKYL HALIDES

Haloalkanes when heated with an ethanolic solution of NH_3 in a sealed tube at 373 K form a mixture of 1°, 2°, and 3° amines along with 4° ammonium salts.

- $\text{R}-\text{X} + \text{H}-\text{NH}_2 \xrightarrow[\Delta]{\text{C}_2\text{H}_5\text{OH}} \text{RNH}_2 + \text{HX}$
1° amine
- $\text{RNH}-\text{X} + \text{H}-\text{NH}_2 \xrightarrow[\Delta]{\text{C}_2\text{H}_5\text{OH}} \text{R}-\text{NH}-\text{R} + \text{HX}$
2° amine
- $\text{R}_2\text{N}-\text{X} + \text{H}-\text{NH}_2 \xrightarrow[\Delta]{\text{C}_2\text{H}_5\text{OH}} \text{R}_3\text{N} + \text{HX}$
3° amine
- $\text{R}_3\text{N} + \text{X}-\text{R} \xrightarrow[\Delta]{\text{C}_2\text{H}_5\text{OH}} \text{R}_4\text{N}^+ \text{X}^-$
4° salt
- $\text{R}-\text{X} + \text{Na}-\text{SH} \xrightarrow[\Delta]{\text{C}_2\text{H}_5\text{OH}} \text{R}-\text{SH} + \text{NaX}$
Sod. hydrosulphide Thioalcohol
- $\text{R}-\text{X} + \text{Na}-\text{S}-\text{R}' \xrightarrow[\Delta]{\text{C}_2\text{H}_5\text{OH}} \text{R}-\text{S}-\text{R}' + \text{NaX}$
Sod. mercaptide Thioether
- $\text{R}-\text{X} + \text{Na}_2\text{S} \xrightarrow[\Delta]{\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}} \text{R}-\text{S}-\text{R} + 2\text{NaX}$
Sod. sulphide Thioether

3.8.4 WILLIAMSON'S SYNTHESIS

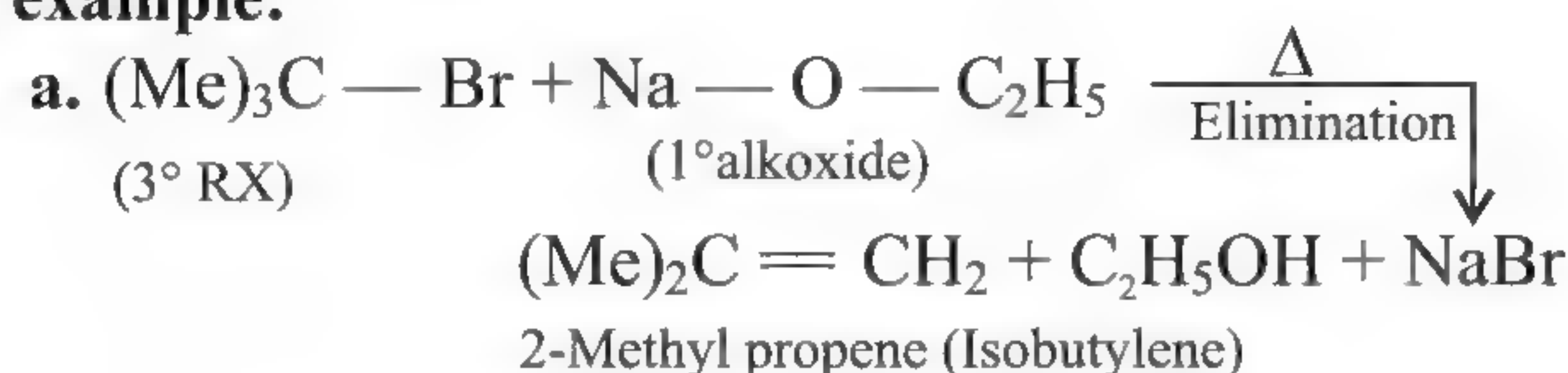


The above reaction is called **Williamson's synthesis**. This reaction involves SN^2 mechanism.

- $\text{R}'\text{O}^- + \text{R}-\text{X} \xrightarrow{\Delta} \text{R}'-\text{O}-\text{R} + \text{X}^-$
- $\text{CH}_3\text{CH}_2\text{O}^- + \text{CH}_3-\text{CH}_2-\text{Br} \xrightarrow{\Delta} \text{CH}_3\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_3 + \text{Br}^-$
- $(\text{Me})_3\text{C}-\text{O}^- + \text{CH}_3-\text{Br} \xrightarrow{\Delta} (\text{Me})_3\text{C}-\text{O}-\text{CH}_3 + \text{Br}^-$
(3° alkoxide) (1° RX)

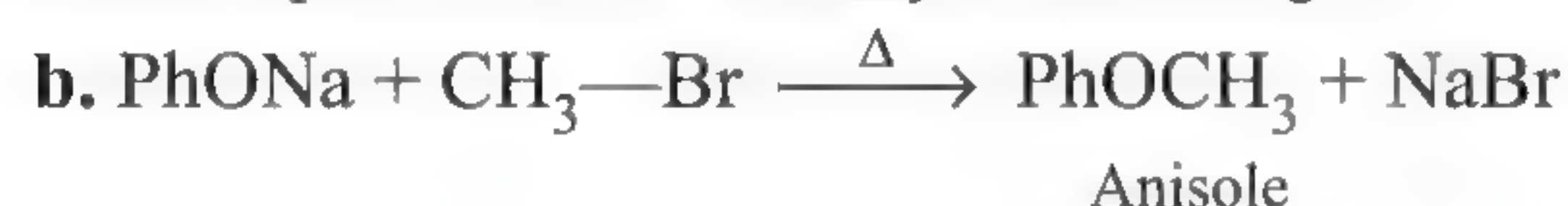
Best yields of unsymmetrical ethers are obtained when alkyl halides are 1° and alkoxides are 3° , since 1° RX are more susceptible to S_N^2 reaction. If RX are 3° and alkoxides are 1° , then the elimination reaction takes place and alkene is obtained.

For example:



With 2° RX, substitution and elimination occur together giving a mixture of ethers and alkenes.

Similarly, phenolic ethers can be easily prepared by treating sodium phenoxide with alkyl halide, e.g.,



However, anisole cannot be prepared by treating bromobenzene with sodium methoxide, since ArX are less reactive towards S_N reaction.

Note: But ethers are formed if ArX contains EWG at *-o-* and *-p-* positions

3.8.5 ETHERS CAN ALSO BE PREPARED BY HEATING RX WITH DRY SILVER OXIDE



3.8.6 ISOMERISATION

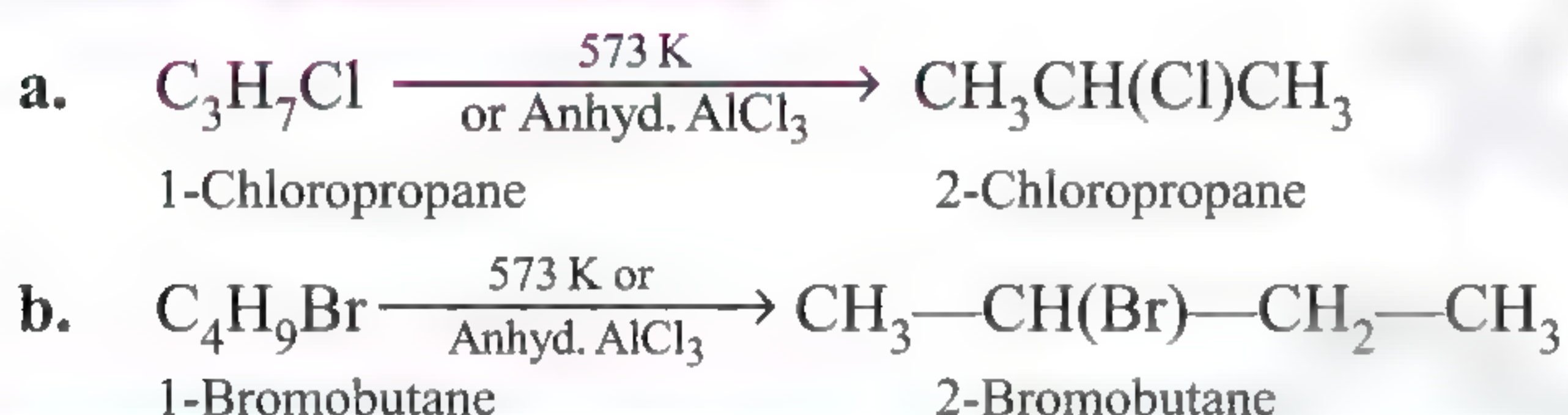


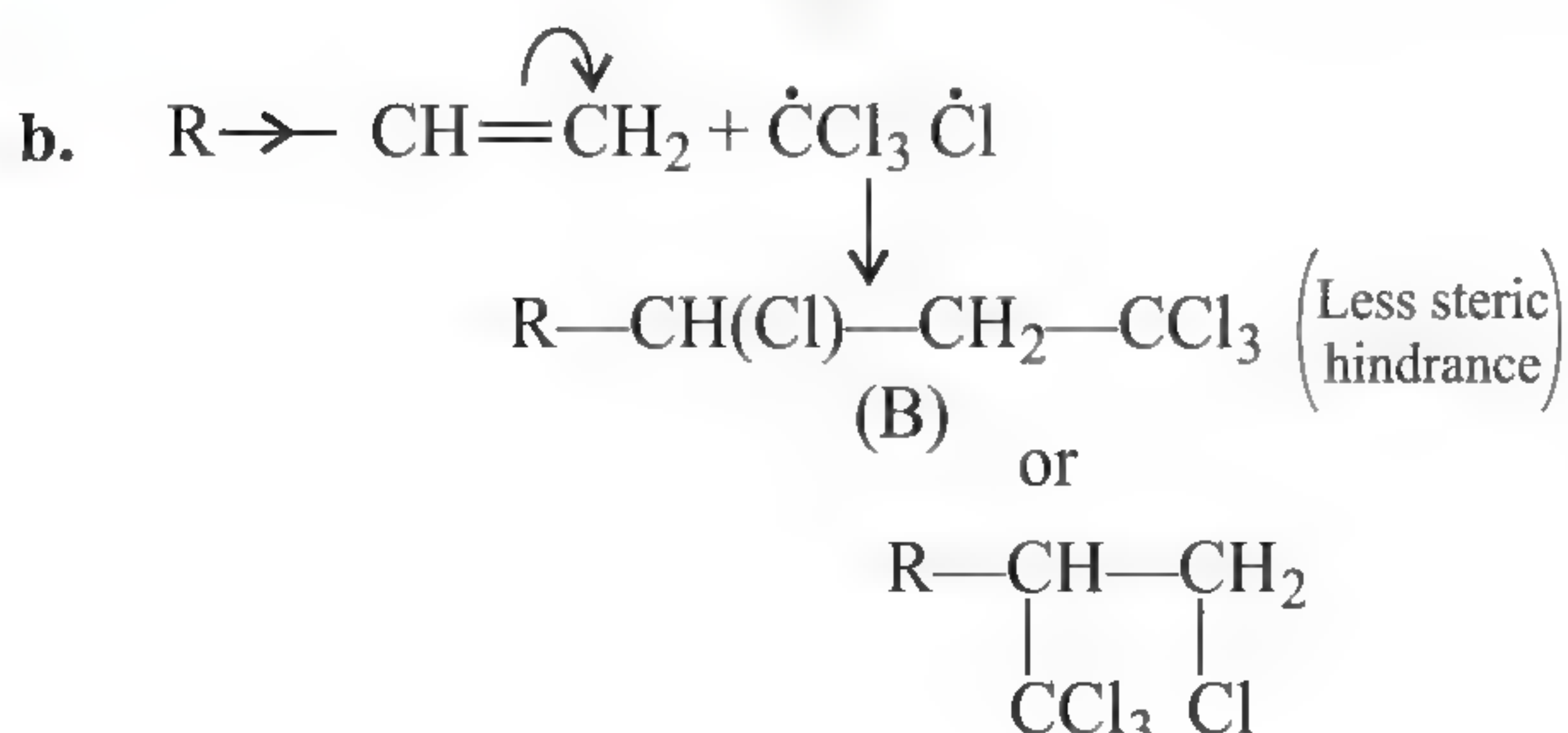
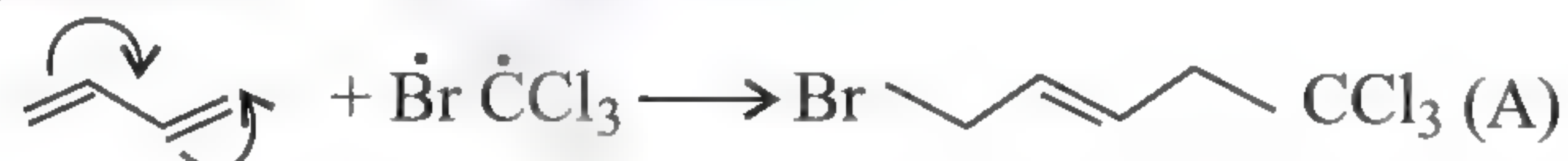
ILLUSTRATION 3.6

Identify (A) to (E).

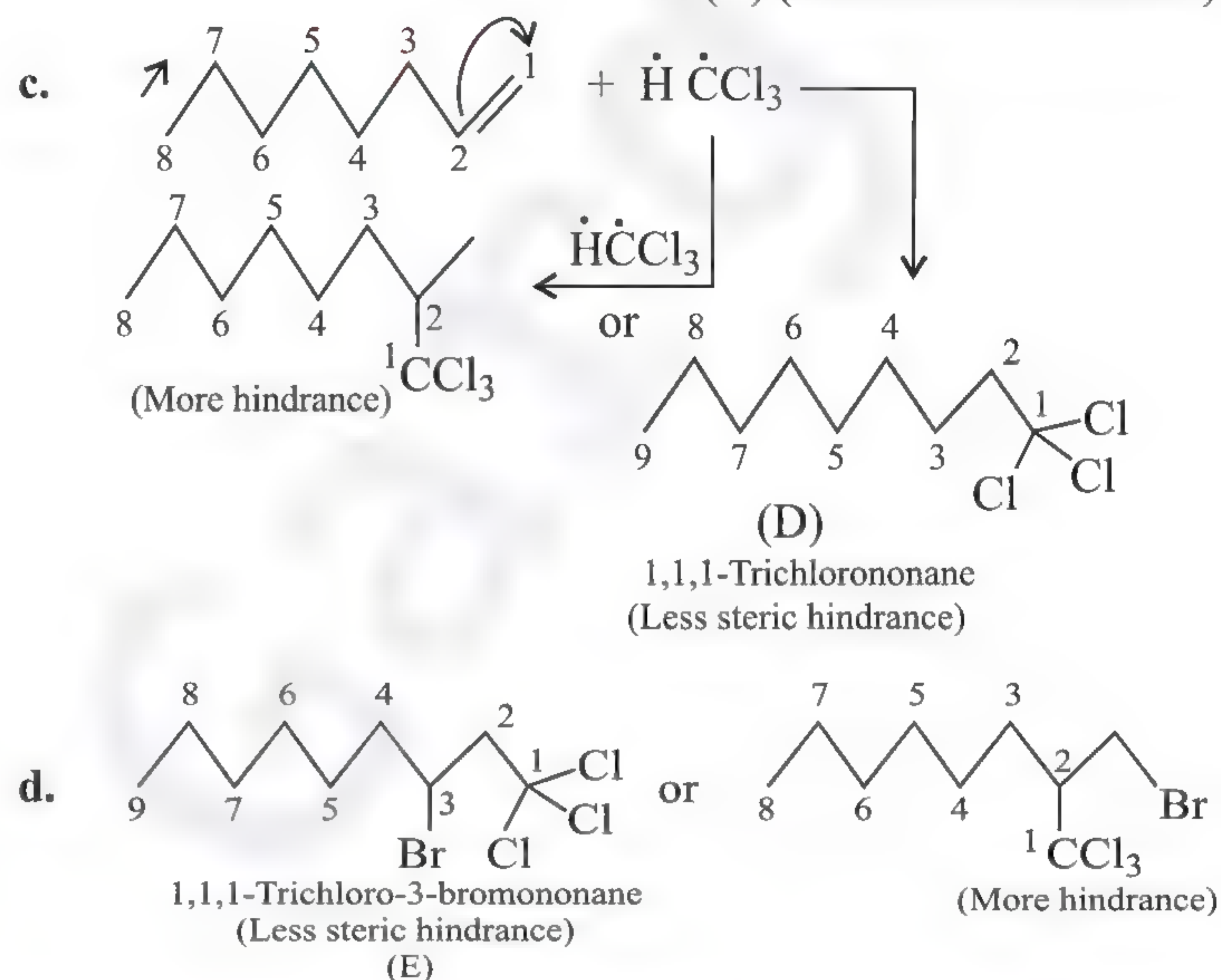
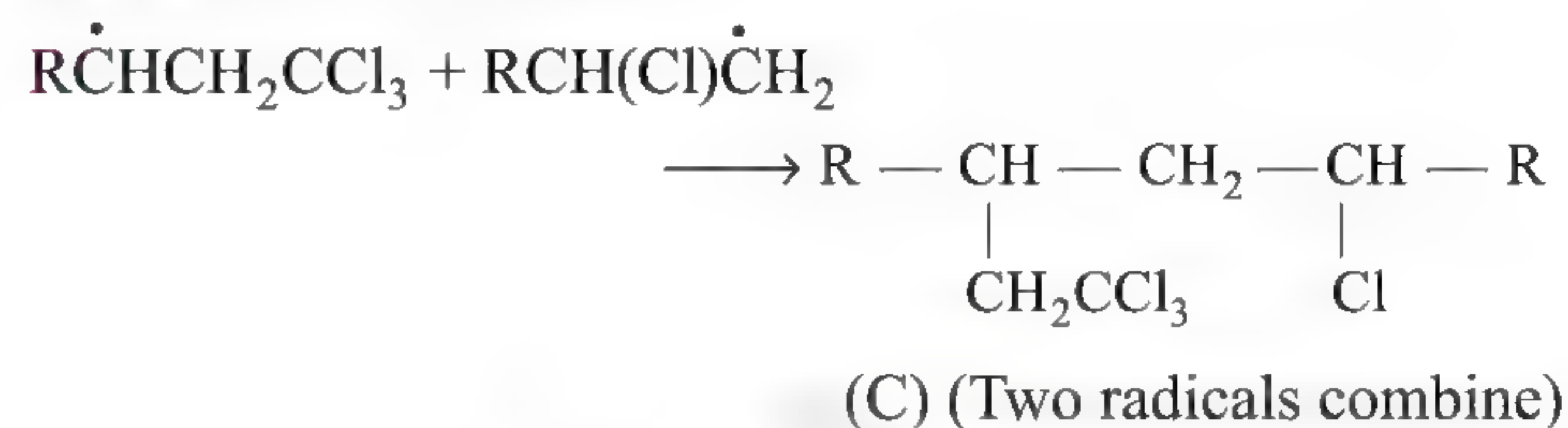
- 1,3-Butadiene + BrCCl_3 + Peroxide \longrightarrow (A)
- $\text{RCH}=\text{CH}_2 + \text{CCl}_4 \xrightarrow{\text{Peroxide}}$ (B) + (C)
- 1-Octene + $\text{CHCl}_3 \xrightarrow{\text{Peroxide}}$ (D)
- 1-Octene + $\text{CBrCl}_3 \xrightarrow{\text{Peroxide}}$ (E)

Sol.

- This is a radical addition which typically gives mainly the 1,4-adduct.



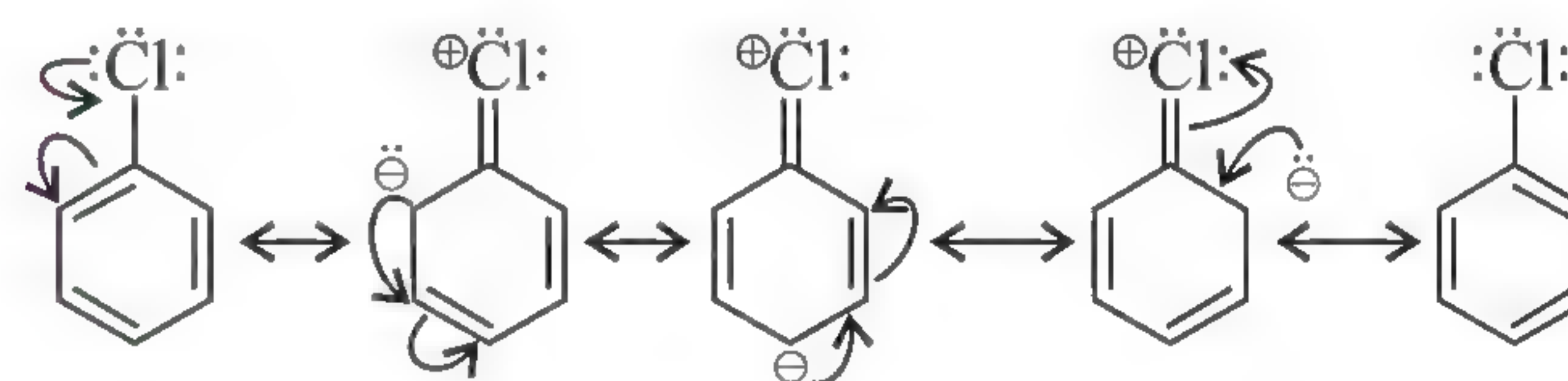
Product (C) can be obtained by the combination of two intermediate free radicals.



3.9 REACTIVITY OF RX AND ArX TOWARDS S_N REACTIONS

Haloarenes, e.g., chlorobenzene, are less reactive than haloalkanes (e.g., CH_3Cl) towards S_N reaction with aq. KOH.

The low reactivity of halogen atom in aryl halides is due to the resonance.



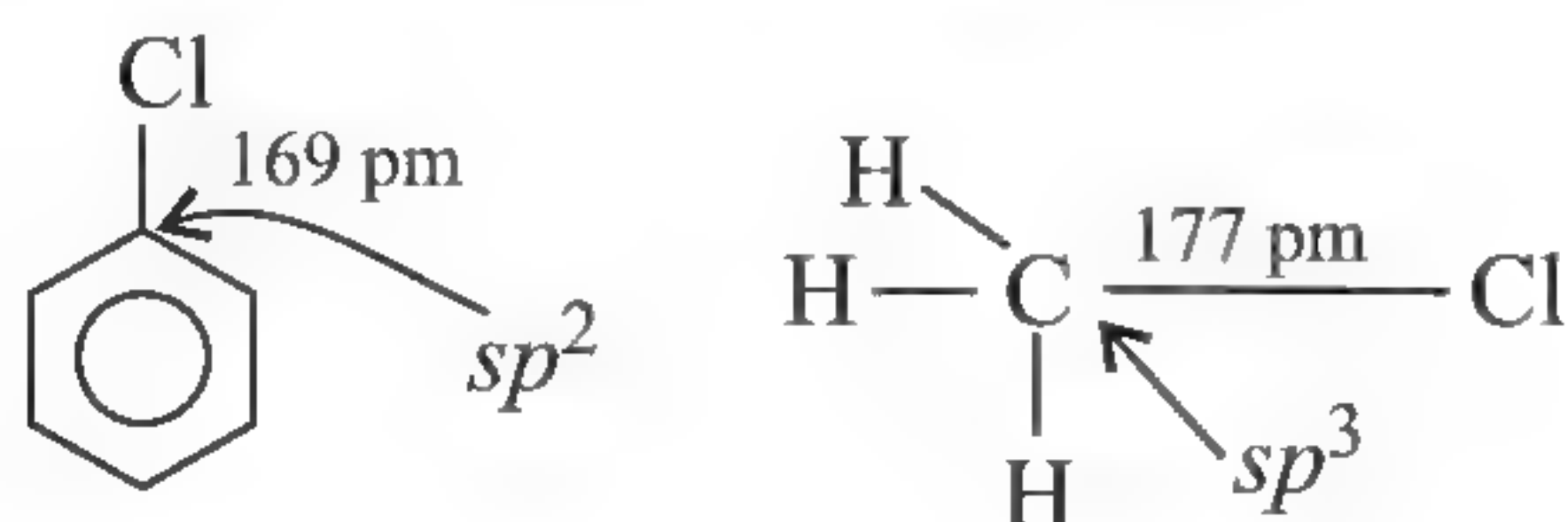
Halogen atom, e.g., Cl atom, has both $-I$ and $+R$ effects, but $+R > -I$ effect. So, due to $+R$ effect of Cl atom, chlorobenzene is resonance stabilised as shown.

- As a result, the (C—Cl) bond acquires partial double bond character; hence it becomes shorter and stronger and thus cannot be easily replaced by nucleophiles, such as $-\text{OH}$, $-\text{NH}_2$, $-\text{CN}$, etc. However, aryl halides can be made to undergo nucleophilic substitution either under drastic conditions (such as the use of high temperature, pressure, or very strong nucleophile) or by the presence of \bar{e} -withdrawing group (e.g., $-\text{NO}_2$, $-\text{COOH}$, etc.) in the *-o-* and *-p-* positions to the nuclear halogen.
- On the other hand, in case of alkyl halides (say CH_3Cl), carbon is attached to chlorine by pure single bond. Consequently, the (C—Cl) bond is weaker and can be easily broken by nucleophiles.

Alternatively:

In chlorobenzene, C atom holding the chlorine atom is sp^2 -hybridised and in methylchloride it is sp^3 -hybridised. Since an

sp^2 -hybridised orbital is smaller in size as compared to an sp^3 -orbital of C, therefore, the (C—Cl) bond in chlorobenzene should be shorter and hence stronger than that in CH_3Cl .

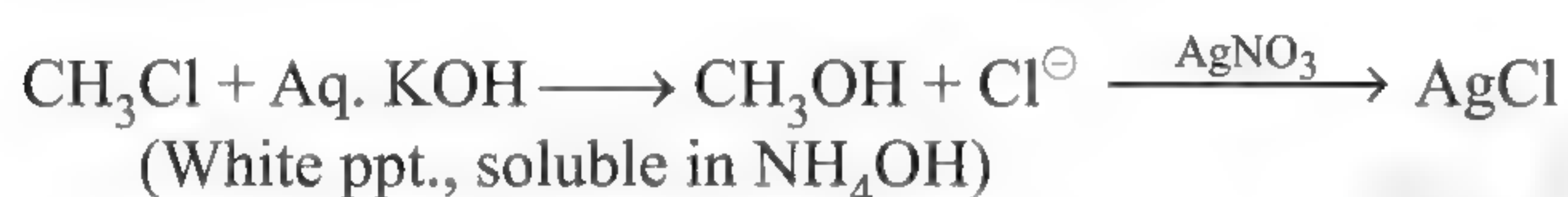
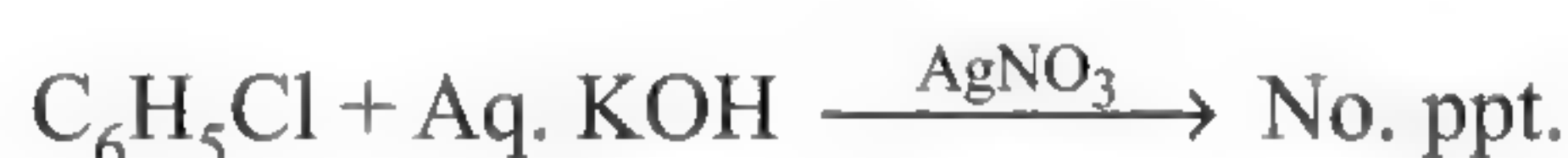


Alternatively:

The sp^2 -hybrid C atom is more EN than an sp^3 -hybrid C atom, therefore, the sp^2 -hybrid C of (C—Cl) bond in aryl halide is less willing to release \bar{e} to the halogen than an sp^3 -hybrid C atom in alkyl halide. As a result, (C—Cl) bond in an aryl halide is less polar, than in alkyl halides. This is supported by the observation that dipole moment of chlorobenzene is 1.7 D as compared to the dipole moment CH_3Cl , i.e., 1.94 D. Consequently, the halogen atom present in aryl halides cannot be easily replaced by nucleophiles.



For the same reason, chlorobenzene does not give test for Cl^- ions when treated with aq. NaOH and then with $AgNO_3$, whereas CH_3Cl gives this test.

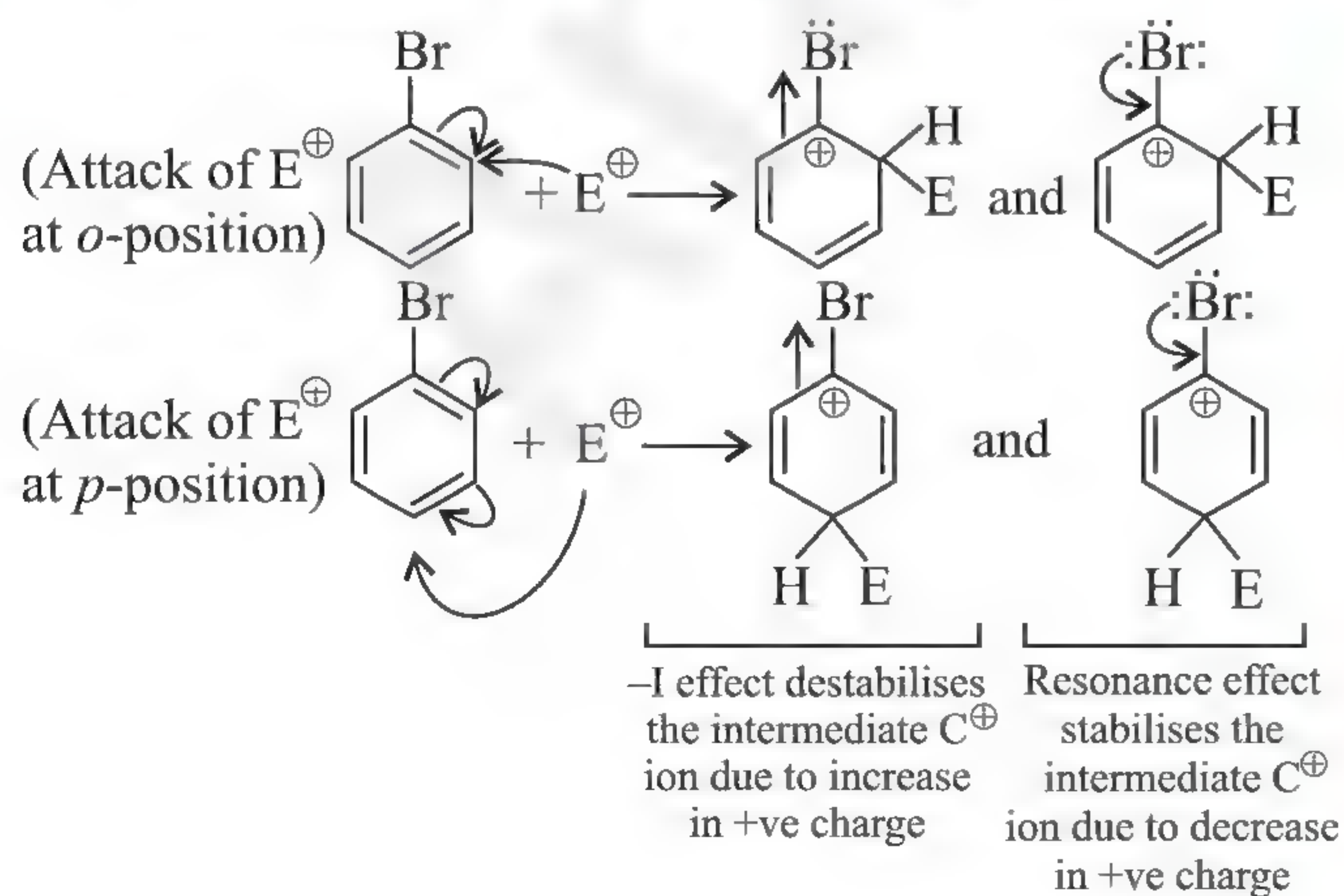


- Instability of phenyl cation: Phenyl cation formed as a result of self-ionisation will not be stabilised by resonance, and therefore, SN^1 mechanism is not possible.
- It is difficult for the \bar{e} -rich nucleophile to approach \bar{e} -rich arenes because of repulsion between them.

ILLUSTRATION 3.7

Although halogens are \bar{e} -withdrawing, yet they are *o*- and *p*-directing towards SE reaction. Why?

Sol. Halogens are said to be π donating but σ withdrawing, i.e., they withdraw \bar{e} 's through $-I$ effect but release \bar{e} 's through resonance. The intermediate carbocation formed during SE reaction is destabilised by the $-I$ effect of the halogens.



Resonance stabilises the intermediate carbocation and this effect is more prominent at *o*- and *p*-positions. $-I$ effect is stronger (due to high EN of halogens) than resonance and causes net \bar{e} withdrawal, and thus causing net deactivation. The resonance effect tends to oppose the inductive effect for the attack at *o*- and *p*-positions and hence makes the deactivation less for *o*- and *p*-substitution.

The reactivity of halogens is controlled by $-I$ effect, and orientation (where E^+ enters *o*, *m*, or *p*) is controlled by resonance effect.

Hence, the reactivity of halogens towards SE reaction is $I > Br > Cl > F$.

That is why the reactivity of haloarenes (e.g., chlorobenzene) is less than that of benzene towards SE reactions. But reaction of chlorobenzene with E^+ takes place at *o*- and *p*-positions. Enthalpy diagram for the reaction of E^+ with $PhBr$ compared to the reaction with benzene also explains the above statement.

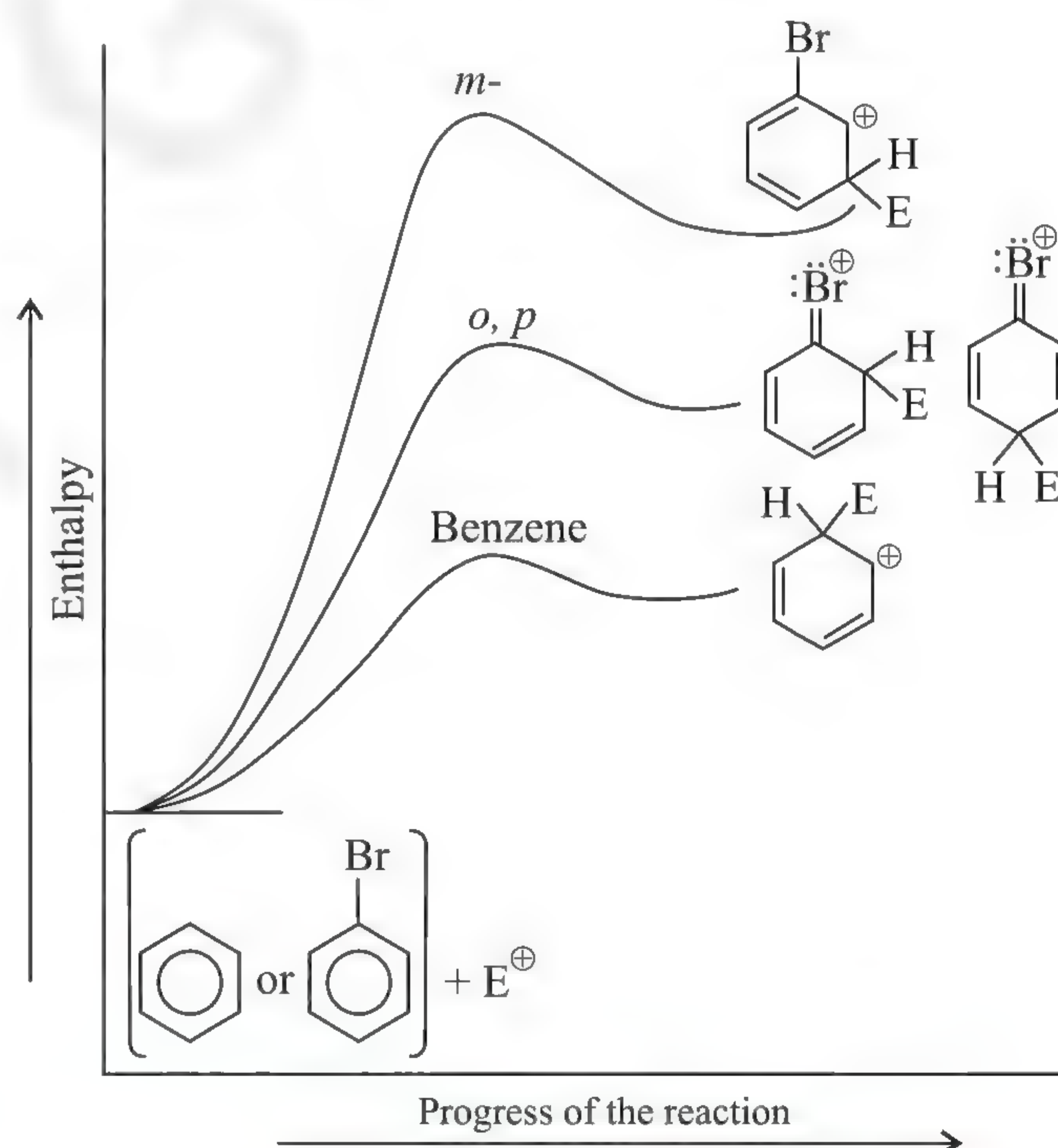


ILLUSTRATION 3.8

Give the decreasing order of the relative reactivity towards SE reaction of the following compounds.

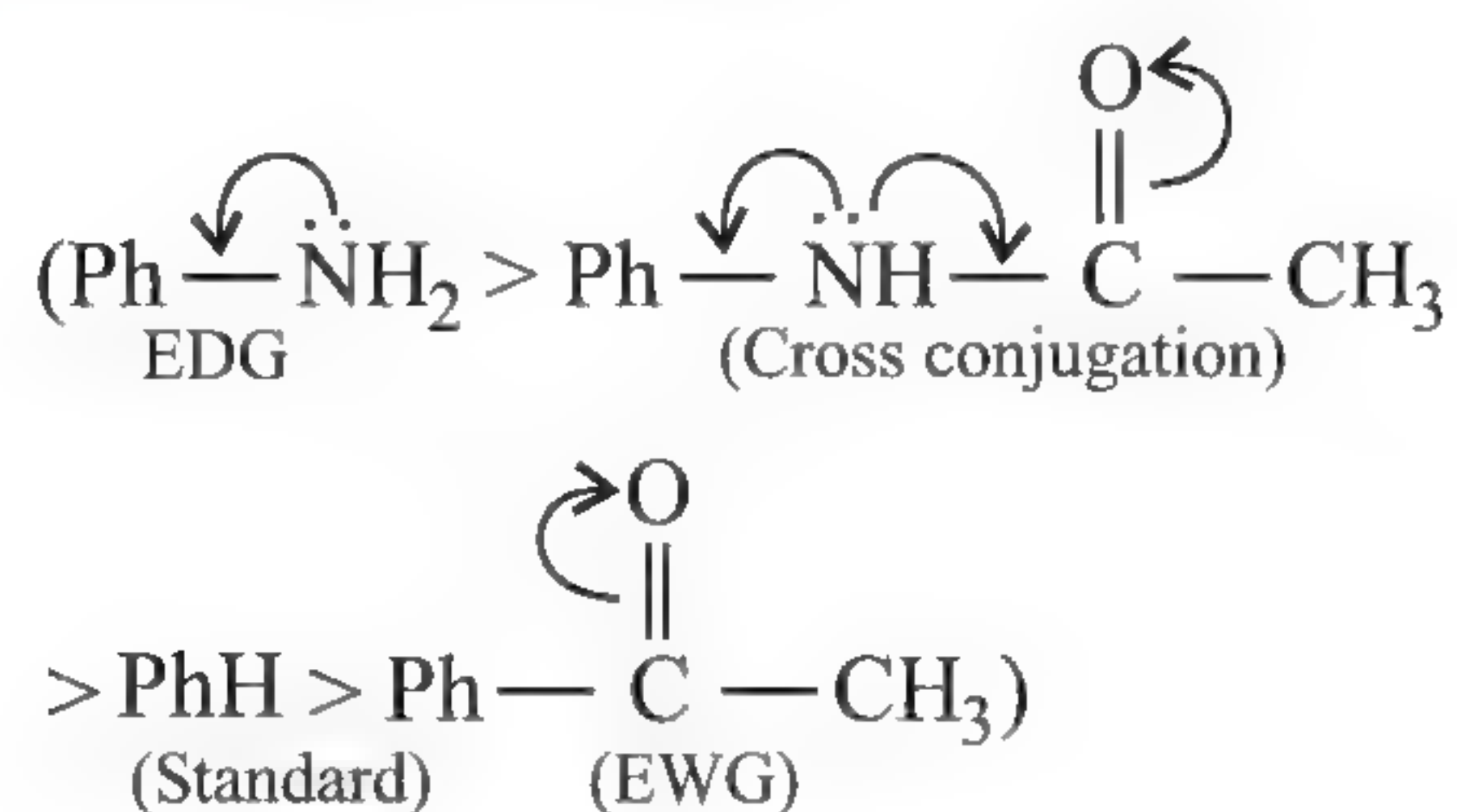
- I. Benzene, II. Phenol, III. Aniline, IV. Chlorobenzene
- I. Acetanilide, II. Aniline, III. Acetophenone, IV. Benzene
- I. 1,3-Dimethyl benzene, II. 1,4-Dimethyl-benzene, III. Toluene, IV. Benzene, V. 1,3,5-Trimethyl benzene
- I. *p*-Methyl benzoic acid, II. Terephthalic acid, III. *p*-Xylene, IV. Toluene
- I. *p*-Xylene, II. *m*-Xylene, III. *p*-Nitrotoluene, IV. *m*-Nitrotoluene, V. Benzene

Sol.

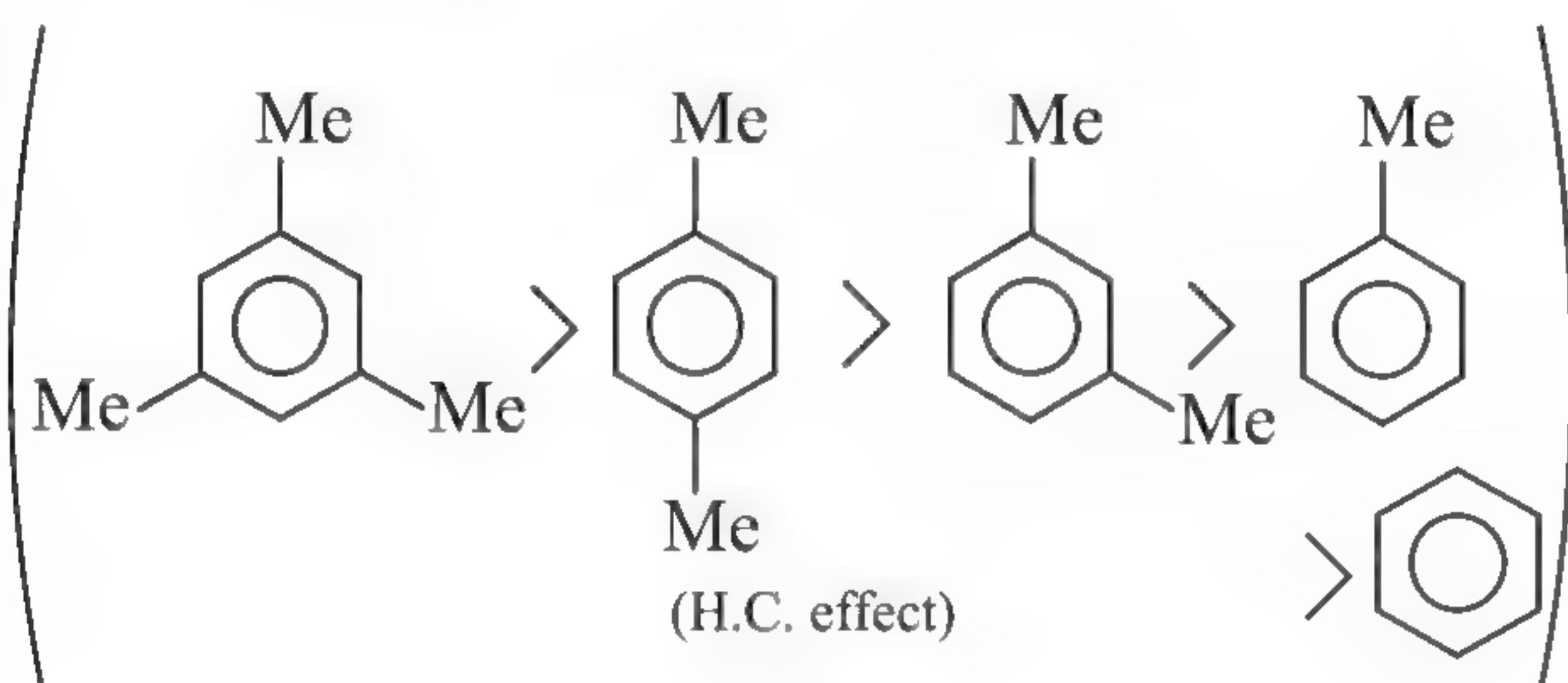
a. (III) > (II) > (I) > (IV) ($\text{PhNH}_2 > \text{PhOH} > \text{PhH} > \text{Ph-Cl}$)

Reactivity order of $-\text{NH}_2 > -\text{OH} > -\text{H} > -\text{Cl}$

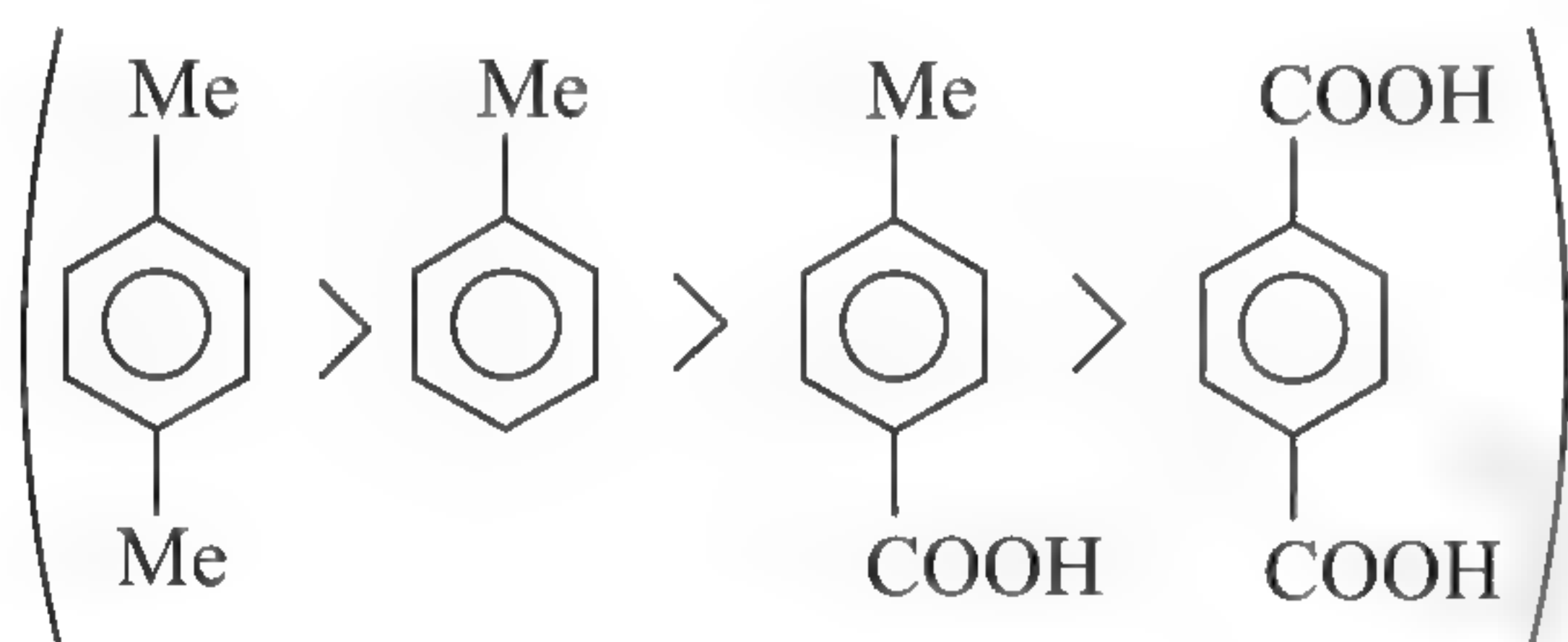
b. (II) > (I) > (IV) > (III)



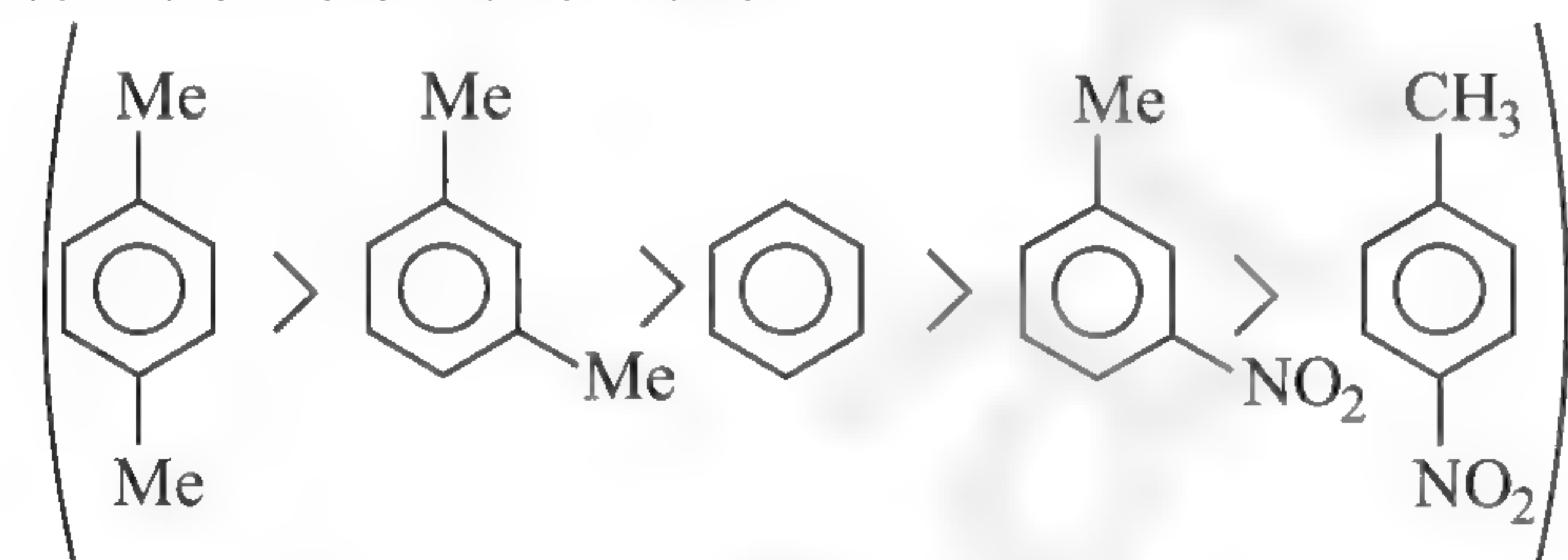
c. (V) > (II) > (I) > (III) > (IV)



d. (III) > (IV) > (I) > (II)



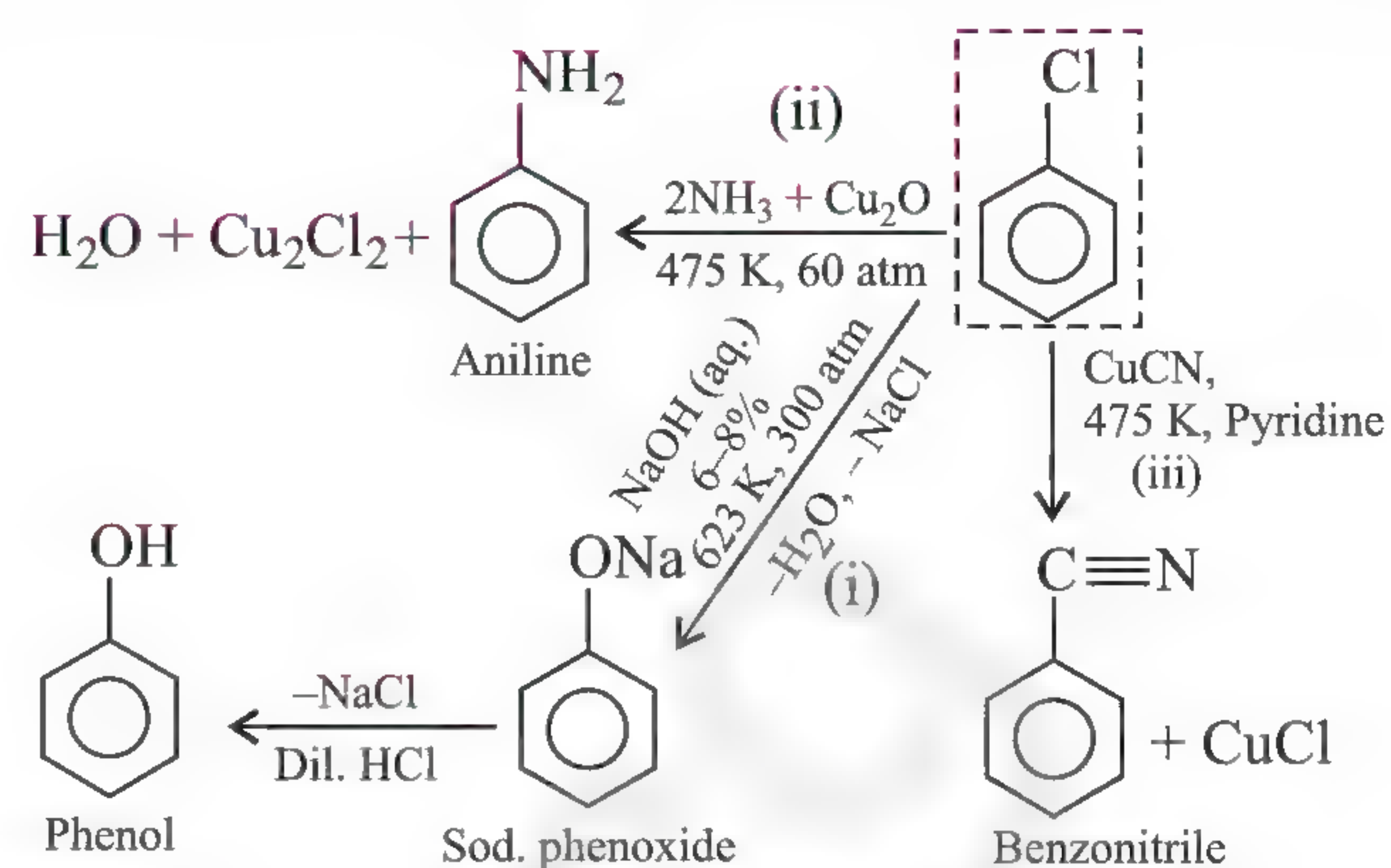
e. (I) > (II) > (V) > (IV) > (III)



Explanation: Hyperconjugative effect is stronger at *o*- and *p*-positions than at *m*-position. So, the reactivity of (I) > (II). \bar{e} withdrawing by resonance of ($-\text{NO}_2$) is stronger at *o*- and *p*-positions than at *m*-position. The deactivating effect is more at *o*- and *p*-positions, so the reactivity of (IV) > (III).

3.10 DOW'S PROCESS

If haloarenes are treated with nucleophiles at higher pressure and temperature or with strong nucleophiles, the (C—Cl) bond can be broken as shown

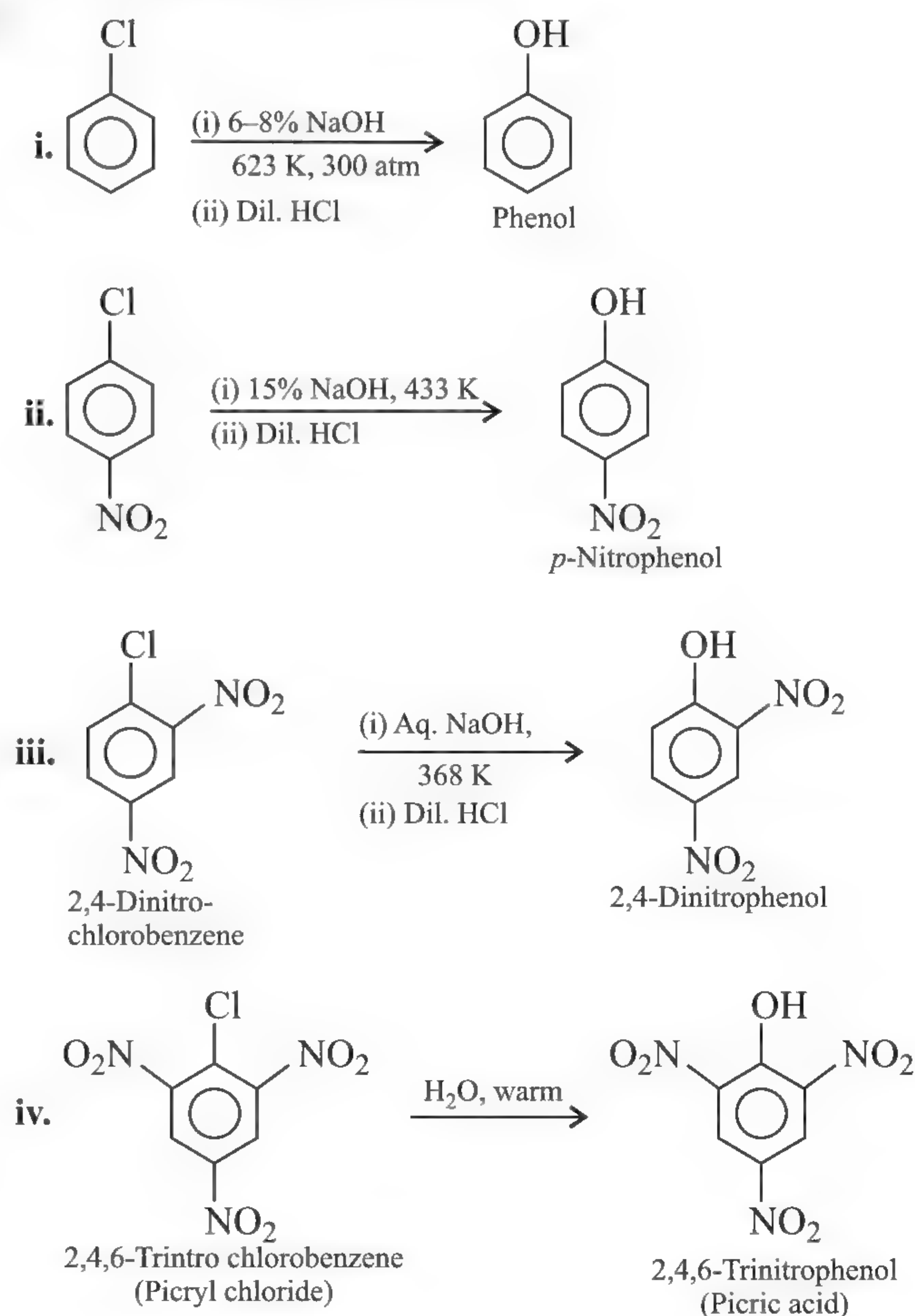


All the reactions take place by ArSN mechanism.

Nucleophiles in (i), (ii), and (iii) are OH^- , NH_2^- , and CN^- , respectively.

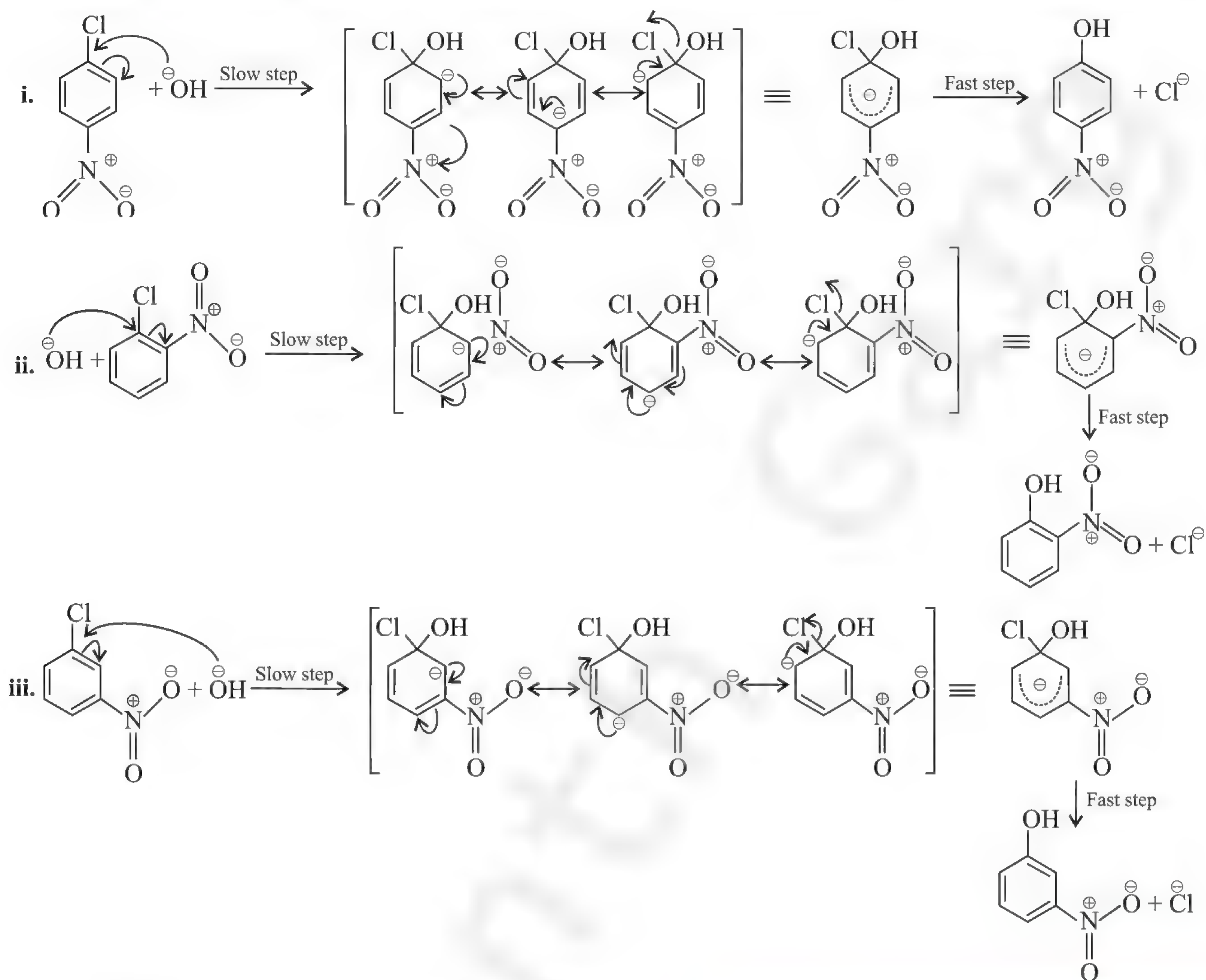
3.11 REACTIVITY OF ALKYL HALIDES IN NUCLEOPHILIC SUBSTITUTION REACTIONS

The replacement of halogens in haloarenes takes place under drastic conditions. Moreover, the presence of \bar{e} -withdrawing groups, such as ($-\text{NO}_2$), ($-\text{COOH}$) groups, at *o*- and *p*-positions (but not at *m*-position) w.r.t. halogen greatly activates the halogen towards nucleophilic displacement. Further, greater the number of such groups at *o*- and *p*-positions w.r.t. the halogen, more reactive are the haloarenes, For example:



3.11.1 EFFECT OF EWG AT ORTHO- AND PARA-POSITION

The effect is pronounced when ($-\text{NO}_2$) group is introduced at *ortho*- and *para*-positions. However, no effect on reactivity of haloarenes is observed by the presence of electron-withdrawing group at *meta*-position. Mechanism of the reaction is as depicted.

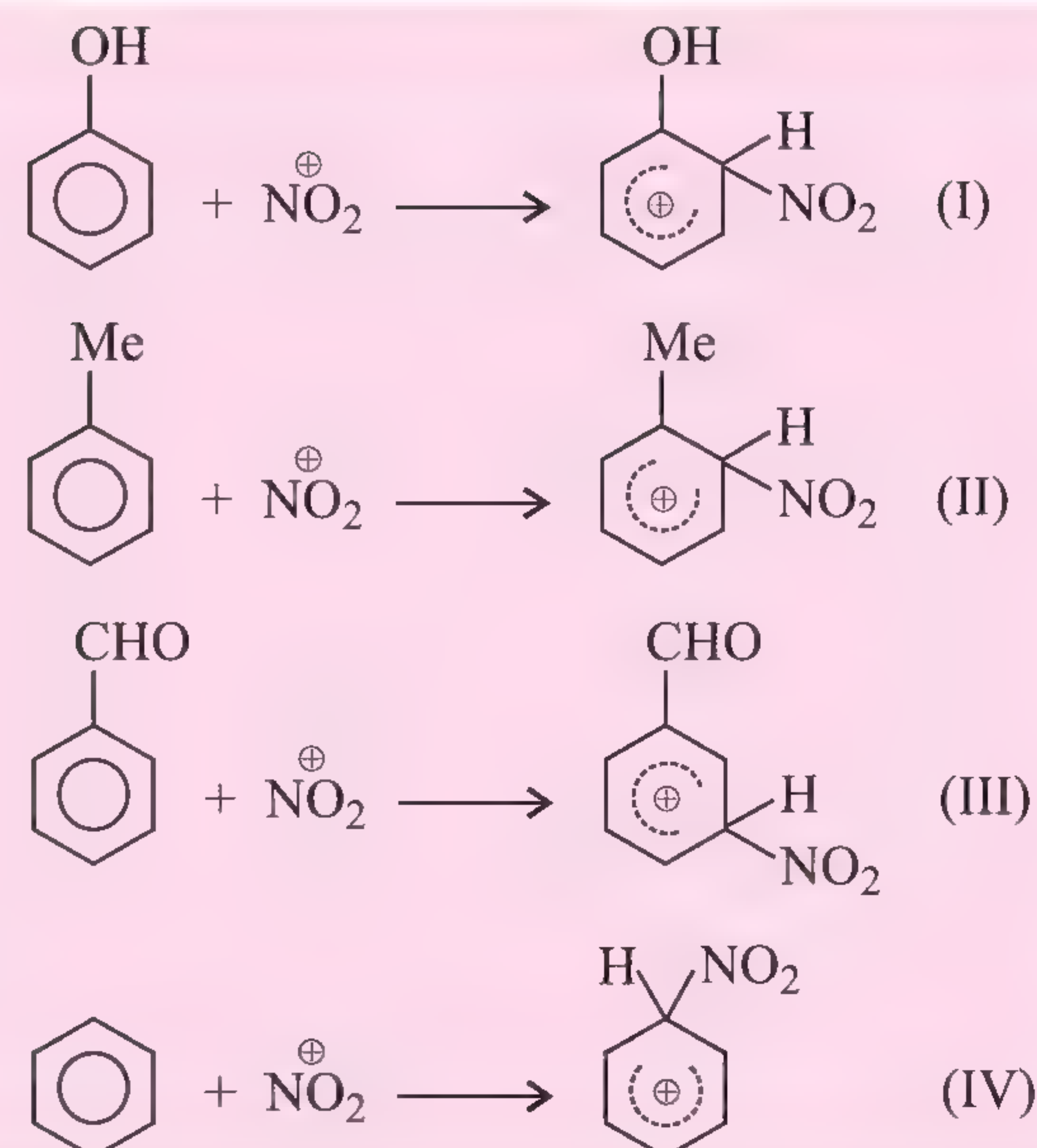


The presence of nitro group at *ortho*- and *para*-positions withdraws the electron density from the benzene ring and thus facilitates the attack of the nucleophile on haloarene. The carbanion thus formed is stabilised through resonance. The negative charge appearing at *ortho*- and *para*-positions with respect to the halogen substituent is stabilised by ($-\text{NO}_2$) group, while in case of *meta*-nitrobenzene, none of the resonating structures bears the negative charge on carbon atom bearing the ($-\text{NO}_2$) group. Therefore, the presence of nitro group at *meta*-position does not stabilise the negative charge and no effect on reactivity is observed by the presence of ($-\text{NO}_2$) group at *meta*-position.

ILLUSTRATION 3.9

Answer the following:

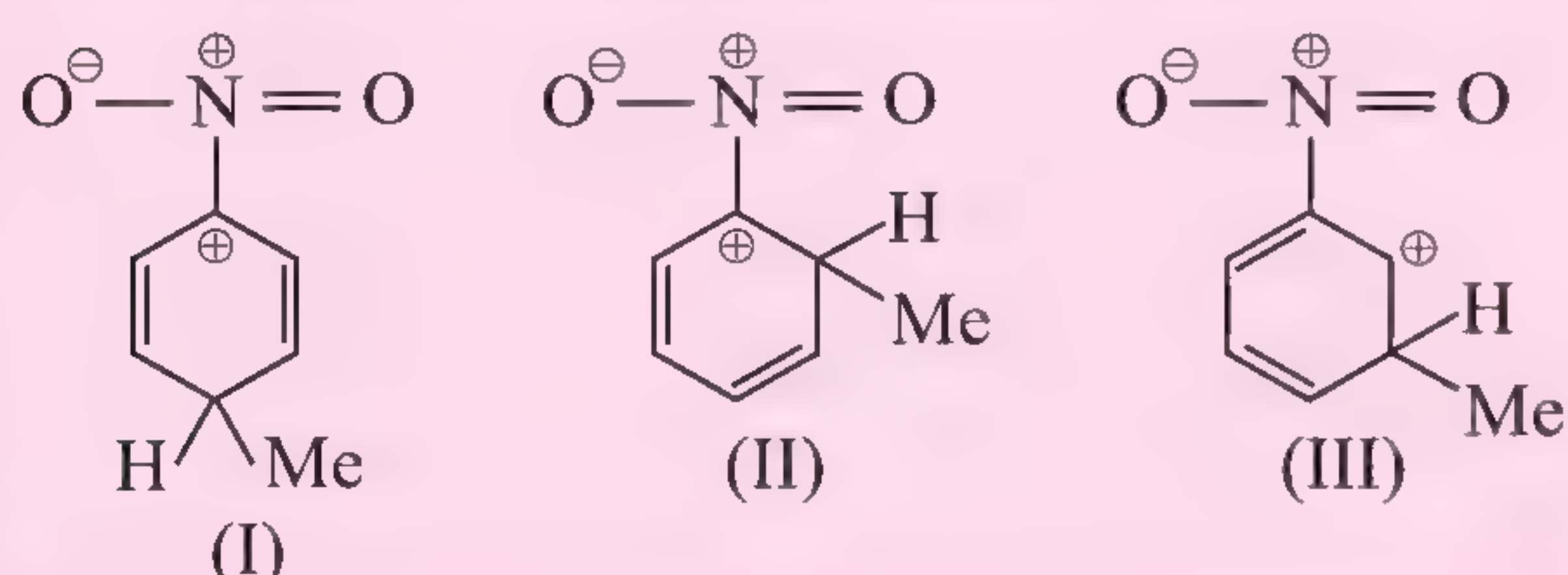
- a. Arrange the following species (I–IV) according to the decreasing order of potential energy.



b. Which of the following is/are stable resonating structures?

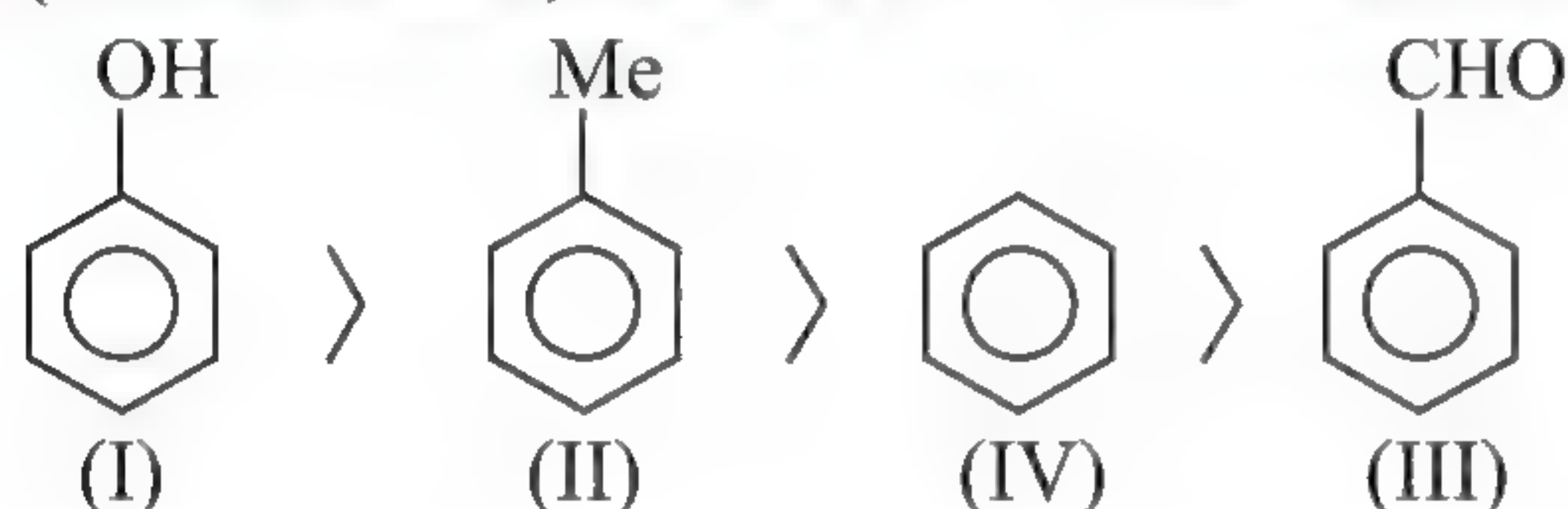


c. Which of the following is/are least stable arenonium ion?

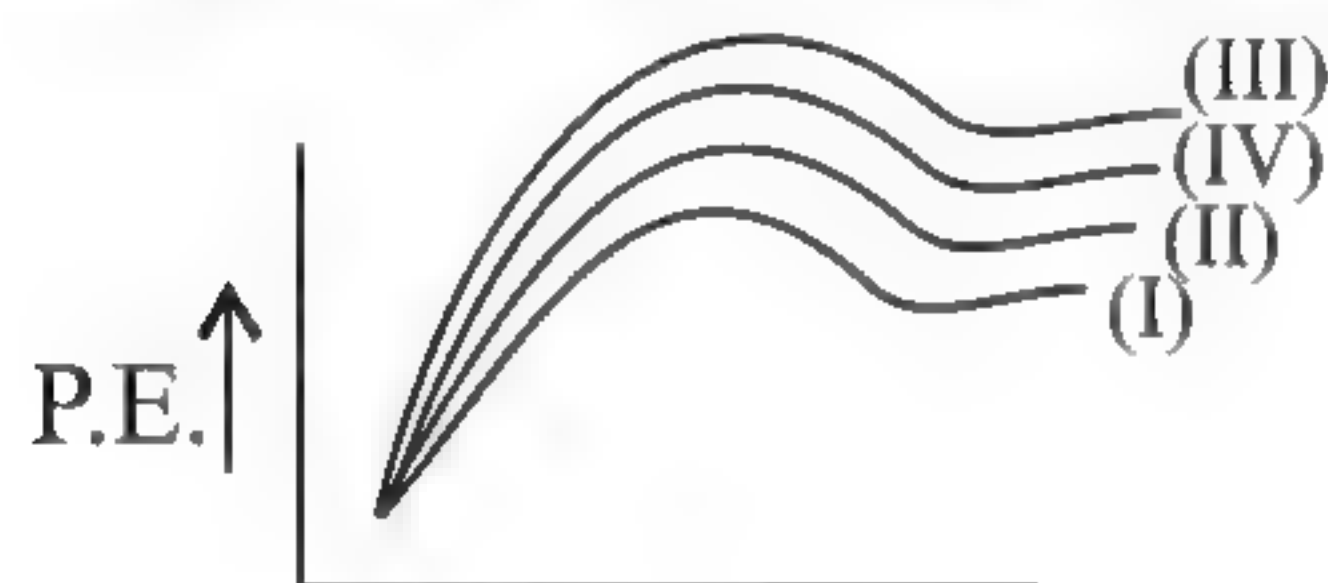


Sol.

a. The reactivity order towards SE reaction is:
(EDG increases, whereas EWG decreases SE reaction.)



Greater the reactivity, more stable is the intermediate species, and lesser the P.E. of the resonating species.



P.E. order is: (I) < (II) < (IV) < (III).

b. None is stable, since the (—OMe) group is *o*, *p*-directing, arenonium ion is stabilised if the attack of E^+ is on *o*- or *p*-position. But in (I), carbocation is formed by *m*-attack.

In (II), (—NO_2) is *m*-directing, and the attack shown is *ortho*. Similarly in (III), ($\text{—C}\equiv\text{N}$) is *m*-directing and the attack shown is at *para*.

c. (I) and (II) are the least stable, since (—NO_2) group is *m*-directing, so carbocation formed by *o*- and *p*-attack is the least stable. Moreover, in (I) and (II) the positive charges are on adjacent C and N. (III) is stable because attack of E^+ is at *meta*.

Sol.

a. In benzene, there is no activating or orienting substituent in present; therefore, halogenation occurs according to the reactivity of halogens $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$ because the E_{act} of halogens is: $\text{F}_2 < \text{Cl}_2 < \text{Br}_2 < \text{I}_2$.

b. In the halogen-substituted benzene, the deactivating or orienting substituents (F, Cl, Br, or I) are present, which direct the incoming E^+ in SE reaction.

The reactivity of halogens in benzene is controlled by $-\text{I}$ effect only, but the orientation (i.e., *o*, *m*, *p*-position) is controlled by $+\text{R}$ effect. Due to $+\text{R}$ effect: they are *o*, *p*-directing.

More the EN of halogens, more the $-\text{I}$ effect and lesser is the reactivity towards SE reaction. (EN order: $\text{F} > \text{Cl} > \text{Br} > \text{I}$). Hence the SE order is: $\text{PhI} > \text{PhBr} > \text{PhCl} > \text{PhF}$.

c. More the EWG, stronger is the acid. The acidic character is determined by the combined effect ($-\text{I}$ and $+\text{R}$). $+\text{R}$ effect of F is more than other halogens due to the overlap of $2p$ of F with $2p$ of C of benzene ring. $-\text{I}$ effect of F is also greatest due to high EN.

The net \bar{e} -withdrawing effect is slightly less than Cl. So the acidic character is in the given order.

$-\text{I}$ effect: $\text{F} > \text{Cl} > \text{Br} > \text{I}$, $+\text{R}$ effect: $\text{F} > \text{Cl} > \text{Br} > \text{I}$,

Net EW effect: $\text{Cl} > \text{F} > \text{Br} > \text{I}$.

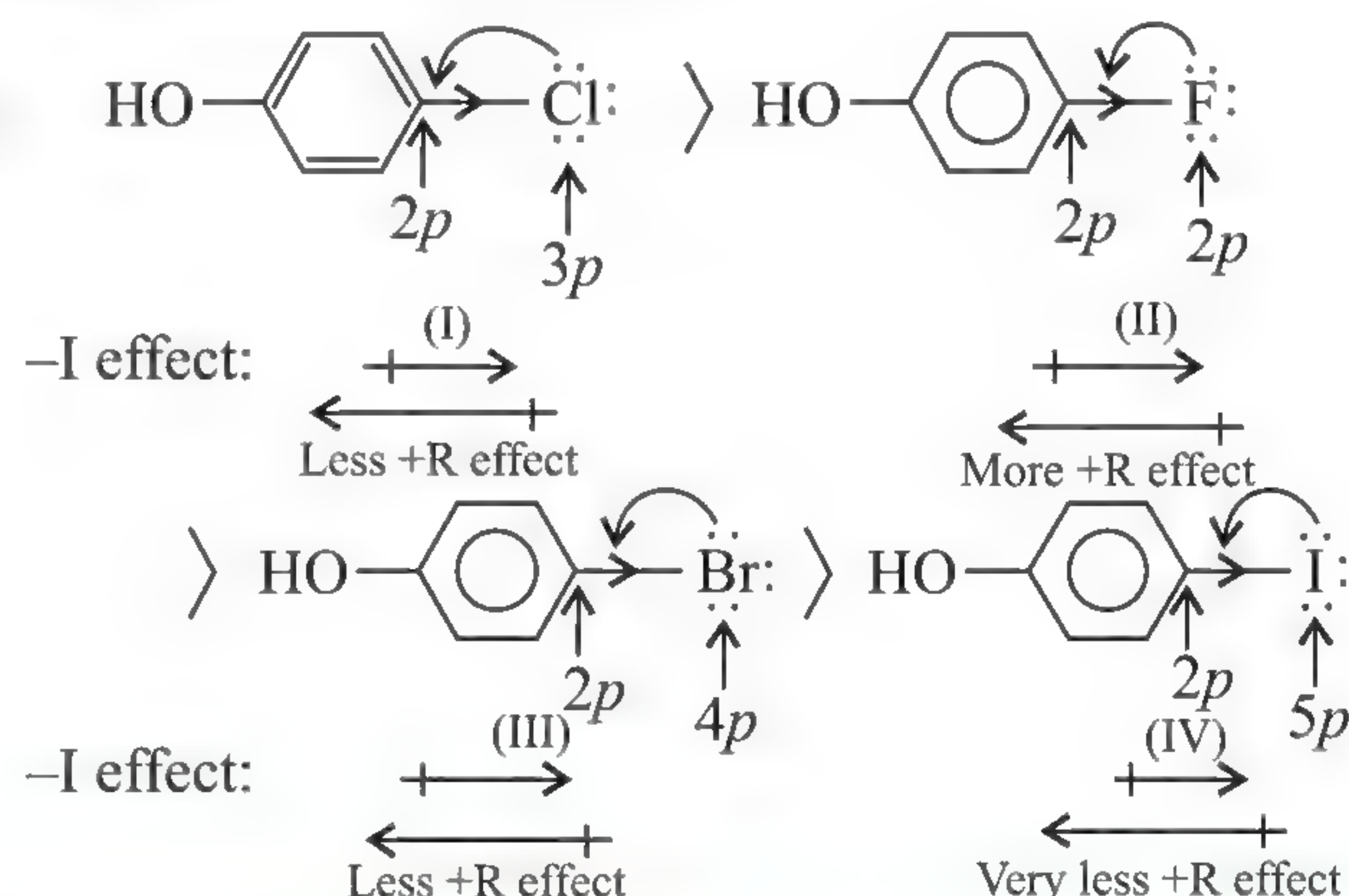


ILLUSTRATION 3.11

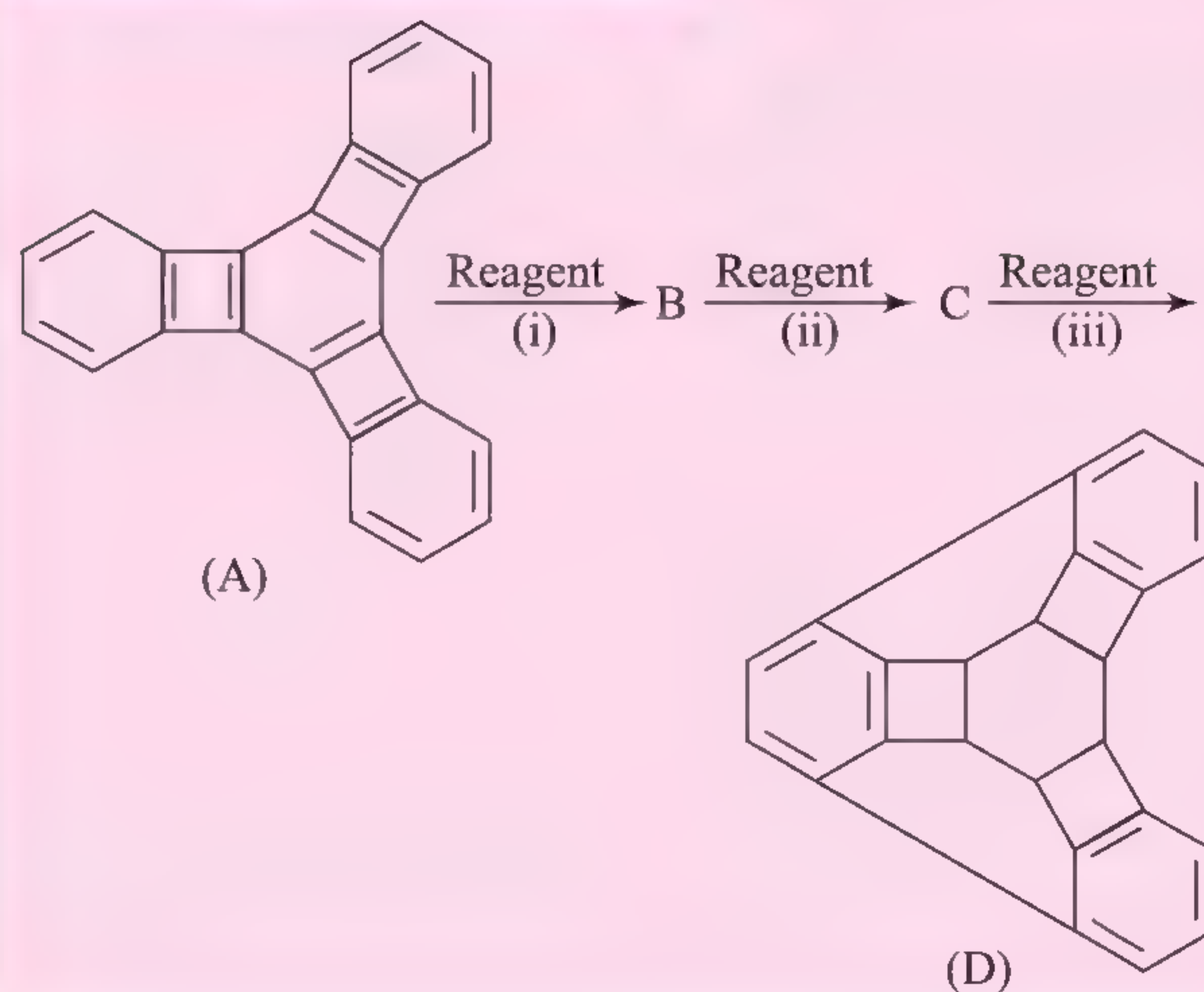
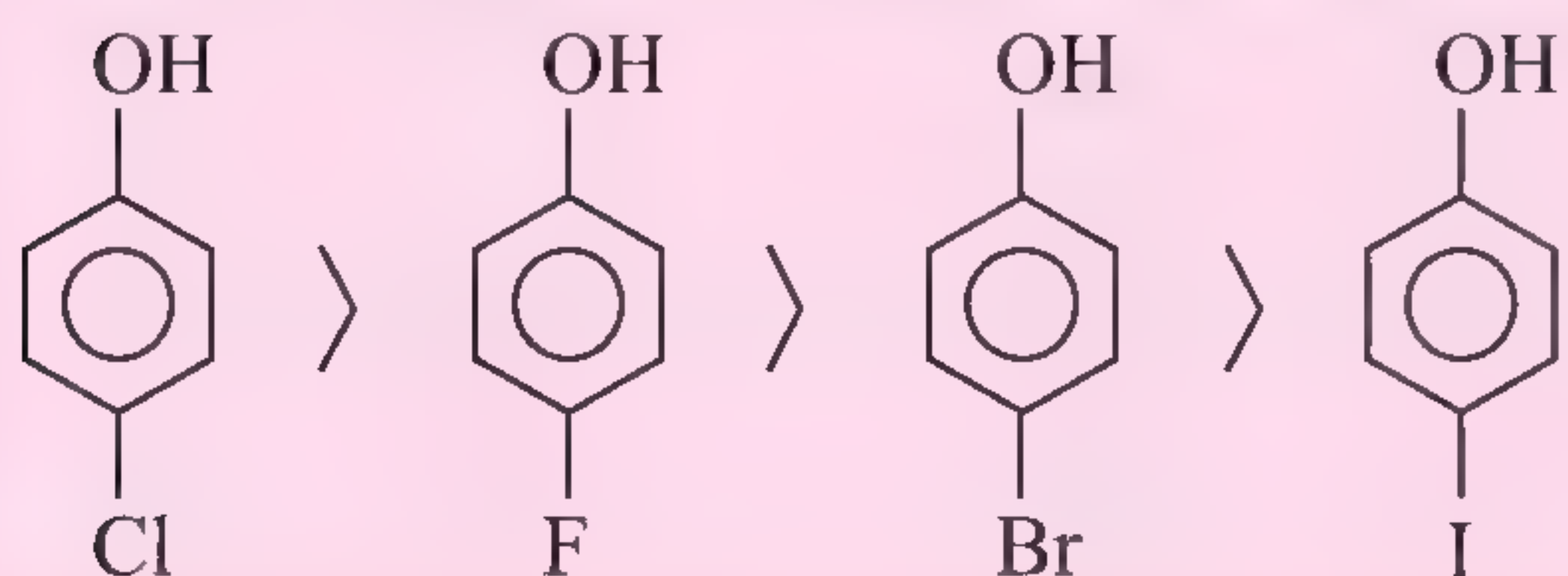


ILLUSTRATION 3.10

Explain the following:

- Reactivity of halogens in the presence of halogen carrier (FeX_3) with benzene is $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$.
- The reactivity of halogen-substituted benzene towards SE reaction is $\text{PhI} > \text{PhBr} > \text{PhCl} > \text{PhF}$.
- The acidic character of halogen-substituted phenol is:

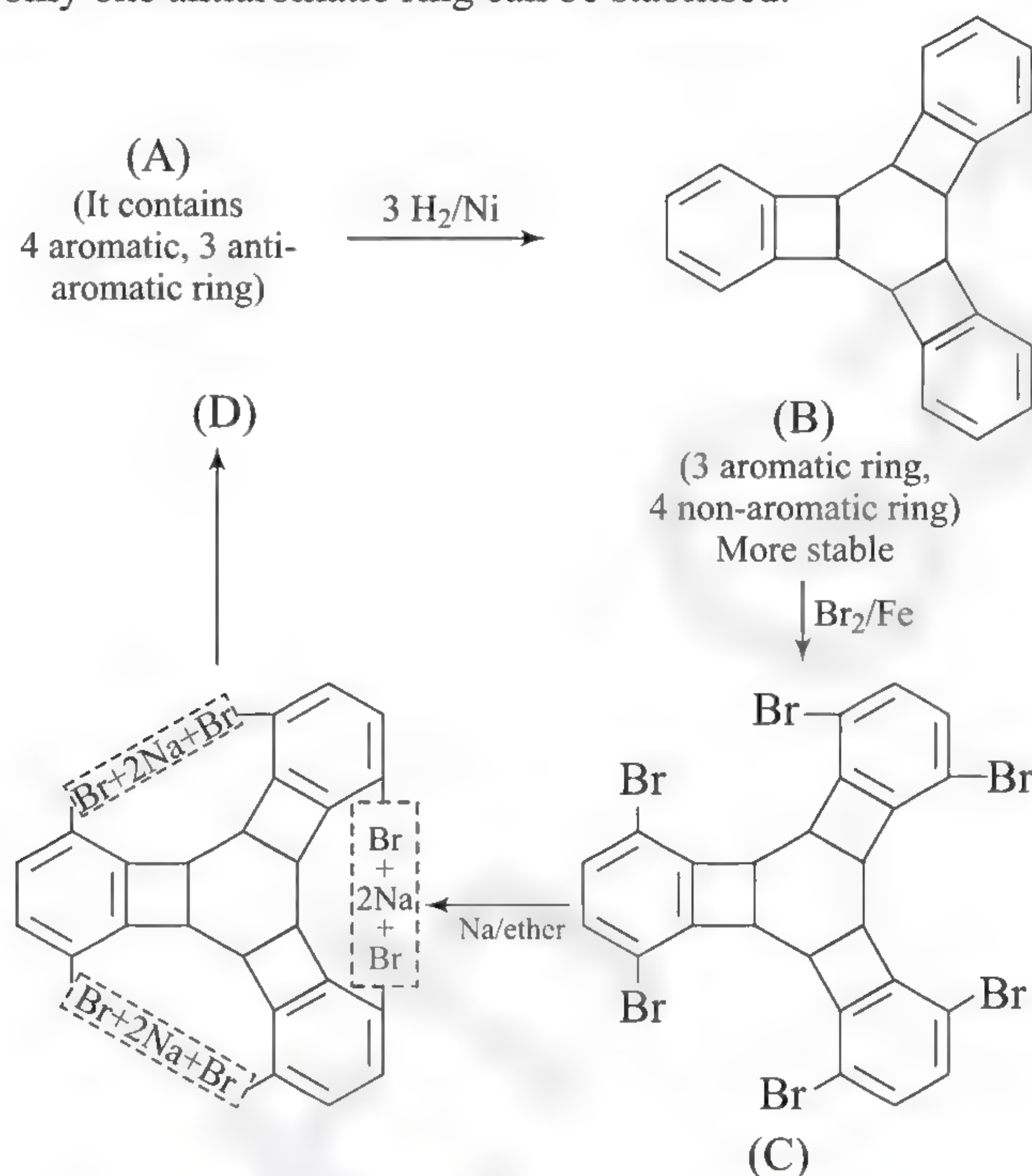


What will be the correct sequence of reagents for above conversions?

- (i) 3 moles of H_2/Ni (ii) Br_2/Fe (iii) Na/Ether
- (i) Na/Ether (ii) Br_2/Fe (iii) 3 moles of H_2/Ni
- (i) Na/Ether (ii) 3 moles of H_2/Ni (iii) Br_2/Fe
- (i) Br_2/Fe (ii) Na/Ether (iii) 3 moles of H_2/Ni

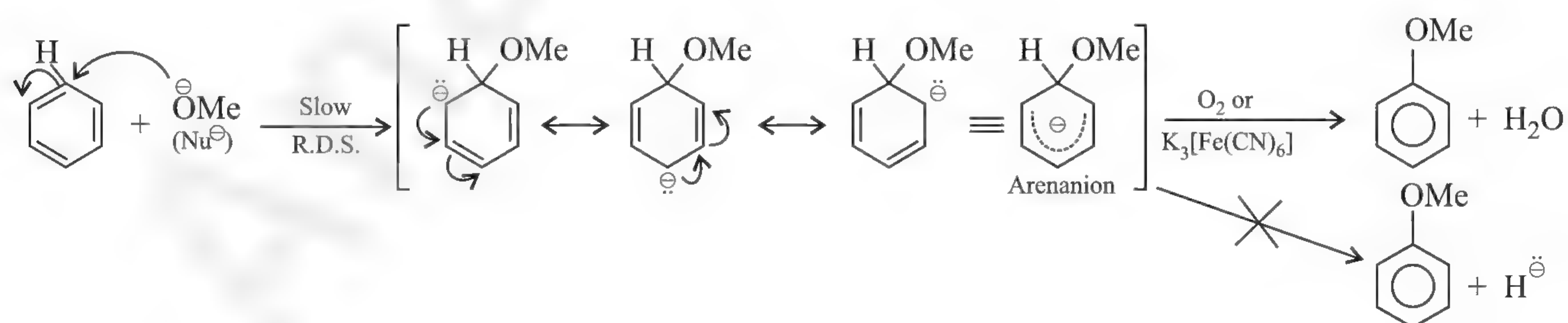
Sol.

- a. Due to reduction of central ring, 3 four membered antiaromatic rings become non-aromatic and thus are stable. If reduction of any one of terminal ring occurs then only one antiaromatic ring can be stabilised.



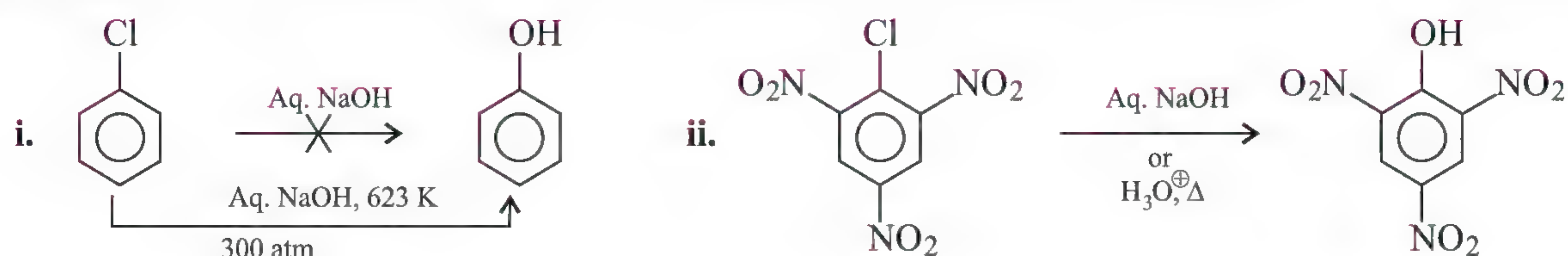
3.12 AROMATIC NUCLEOPHILIC SUBSTITUTION (ArSN) (ADDITION-ELIMINATION) REACTION

- (a) S_N reaction in benzene under ordinary conditions is not possible, since the displacement of H^\ominus , a very strong base and poor leaving group, is very difficult. This can occur only if an oxidant can convert H^\ominus to H_2O . The oxidant O_2 or $\text{K}_3[\text{Fe}(\text{CN})_6]$ can convert H^\ominus to H_2O .



- (b) ArS_N reactions are possible with ArX and ArOTs , aromatic halides and tosylate ($-\text{Ts} = p\text{-Toluene sulphonyl group}$ $\text{Me}-\text{C}_6\text{H}_4-\text{SO}_2-$).

Both $(-\text{X})$ and $(-\text{OTs})$ are good leaving groups, especially when EWG (\bar{e} -withdrawing groups), such as $(-\text{NO}_2)$ and $(-\text{C}\equiv\text{N})$, are present at *ortho* and/or *para* to the reacting C atom, e.g.,



(c) Greater the number of these EWG at *o*- and/or *p*-positions, faster is the reaction and lesser vigorous conditions are required. This is also called **addition-elimination reaction** (since Nu^- adds and $-\text{X}$ eliminates).

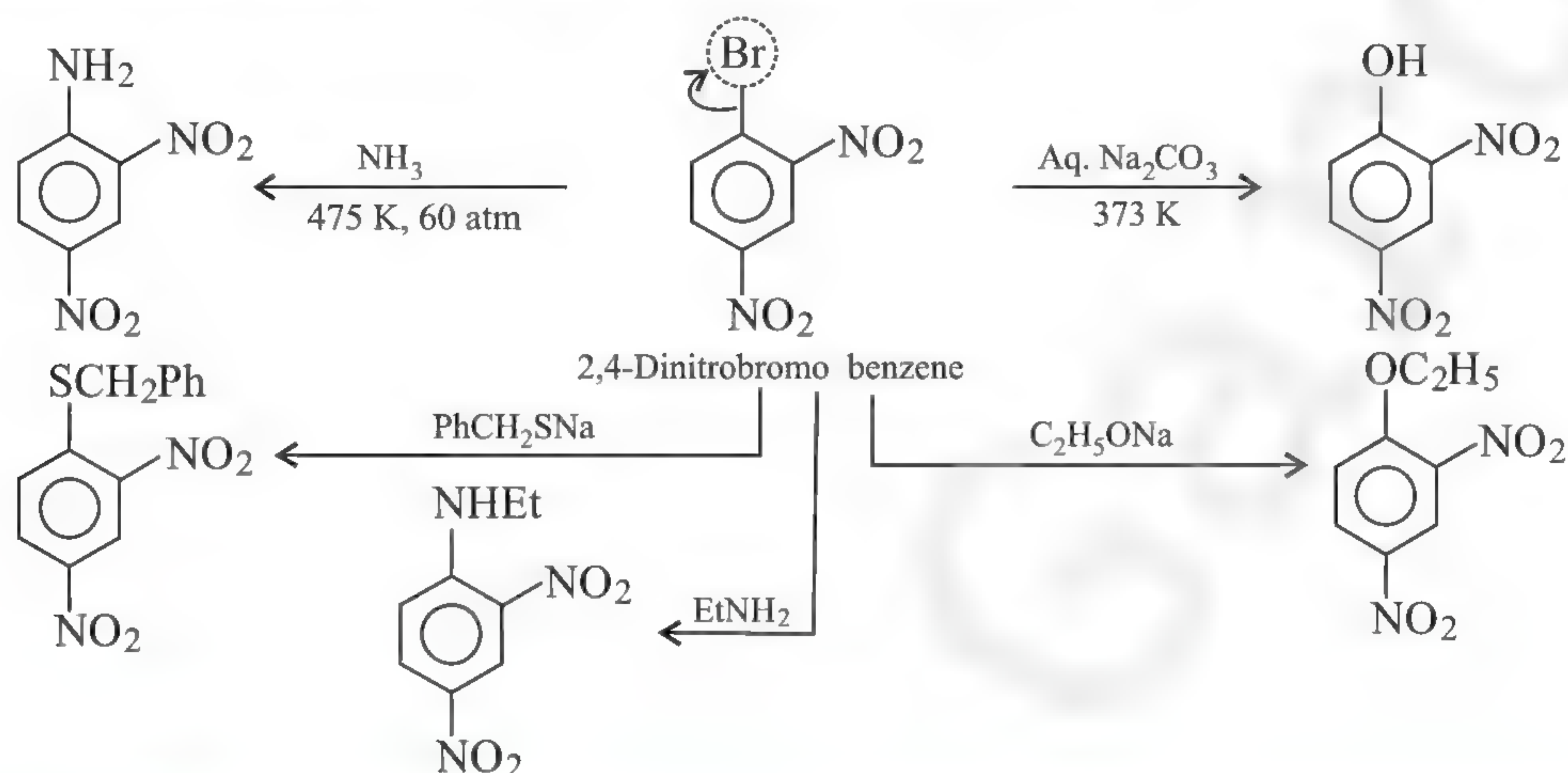
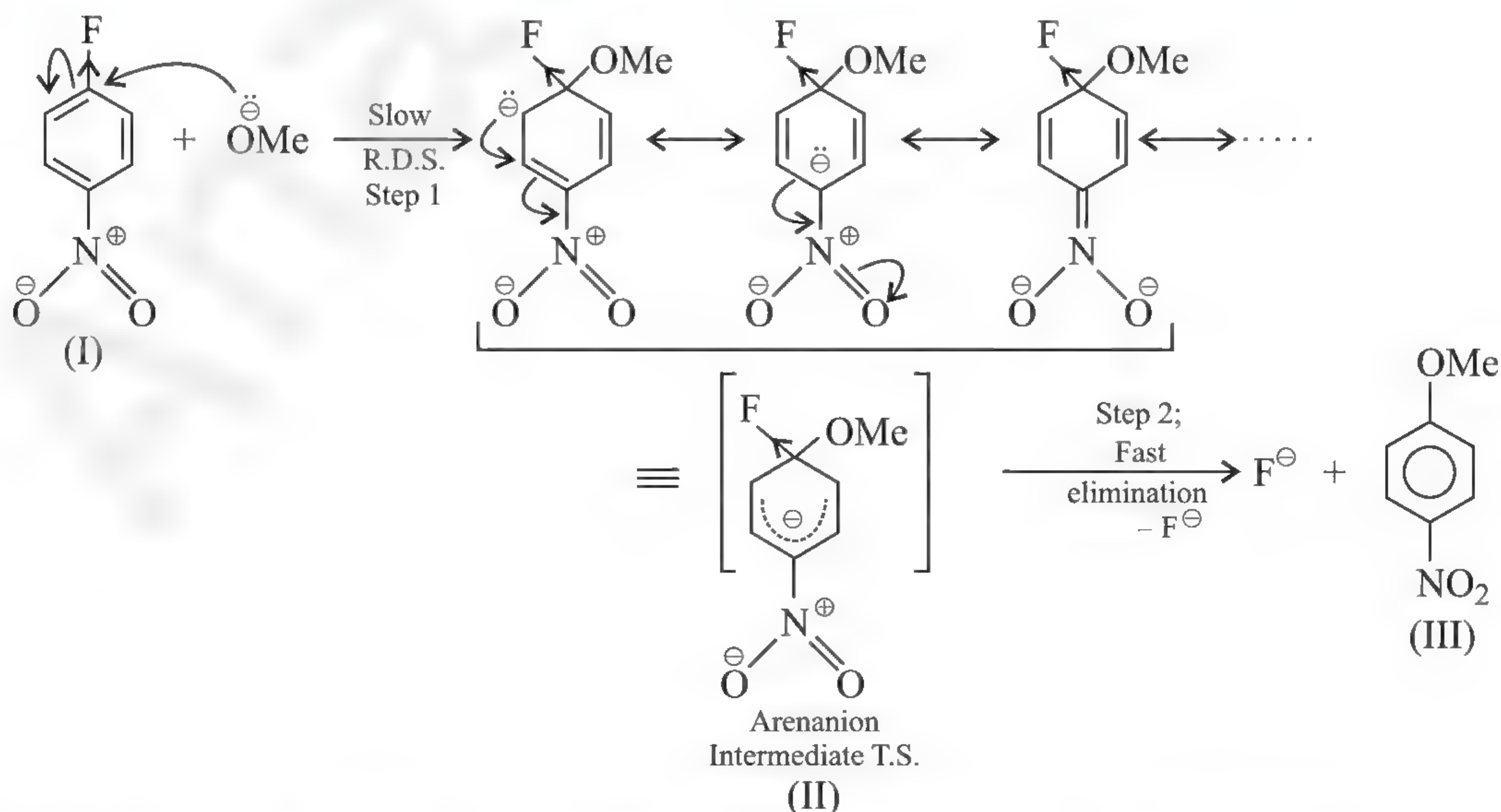


ILLUSTRATION 3.12

For reaction (I) , why is the order of reactivity of halides $\text{ArF} \gg \text{ArCl} > \text{ArBr} > \text{ArI}$, although F^- is a poor leaving group? Explain.

Sol. EN order of halogens: $\text{F} > \text{Cl} > \text{Br} > \text{I}$.

Due to the high EN of F, it stabilises the negative charge more than other halogens on the neighbouring C atoms in the transition and intermediate states.



This also suggests that step 1 is slow and R.D. If step 2 would have been R.D., then the reactivity of ArF would have been the lowest, since F^- is the weakest leaving group of the halide ions; step 2 is fast since (II) (non-aromatic) changes to (III) (aromatic).

$$\therefore \text{Rate} = K[\text{I}][\text{OMe}]$$

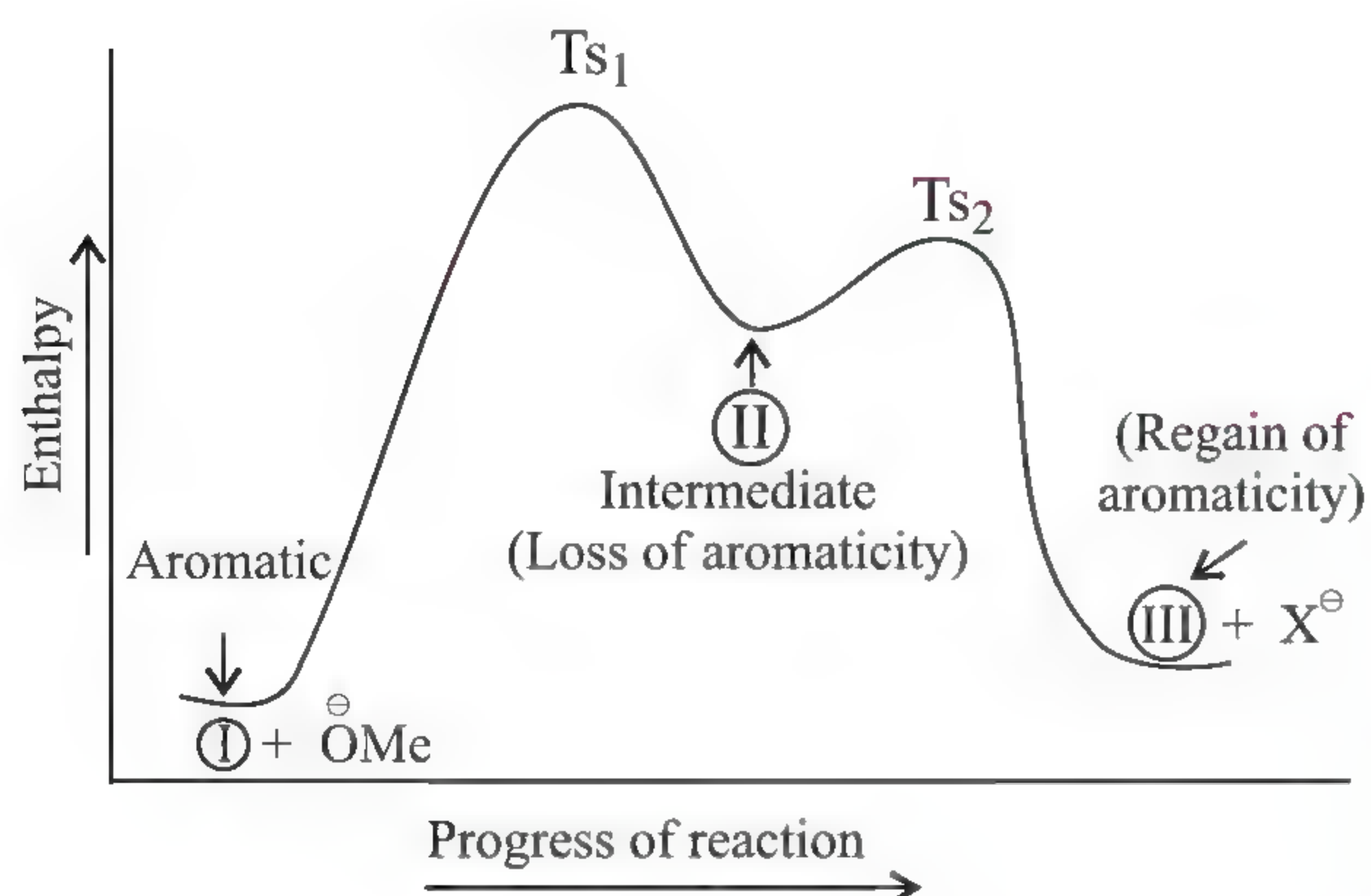
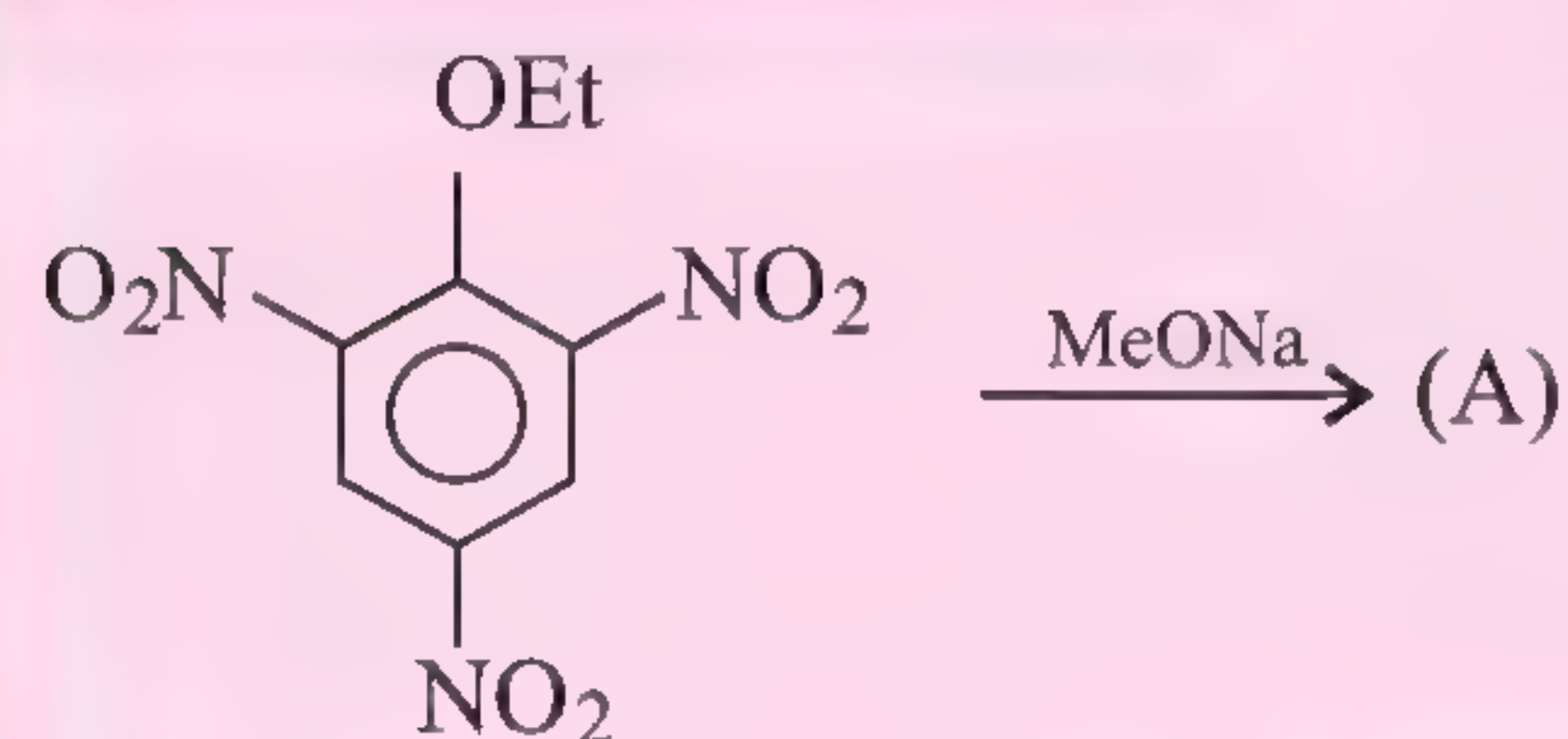


ILLUSTRATION 3.13



Write the structure of (A) and its resonance structures.

Sol.

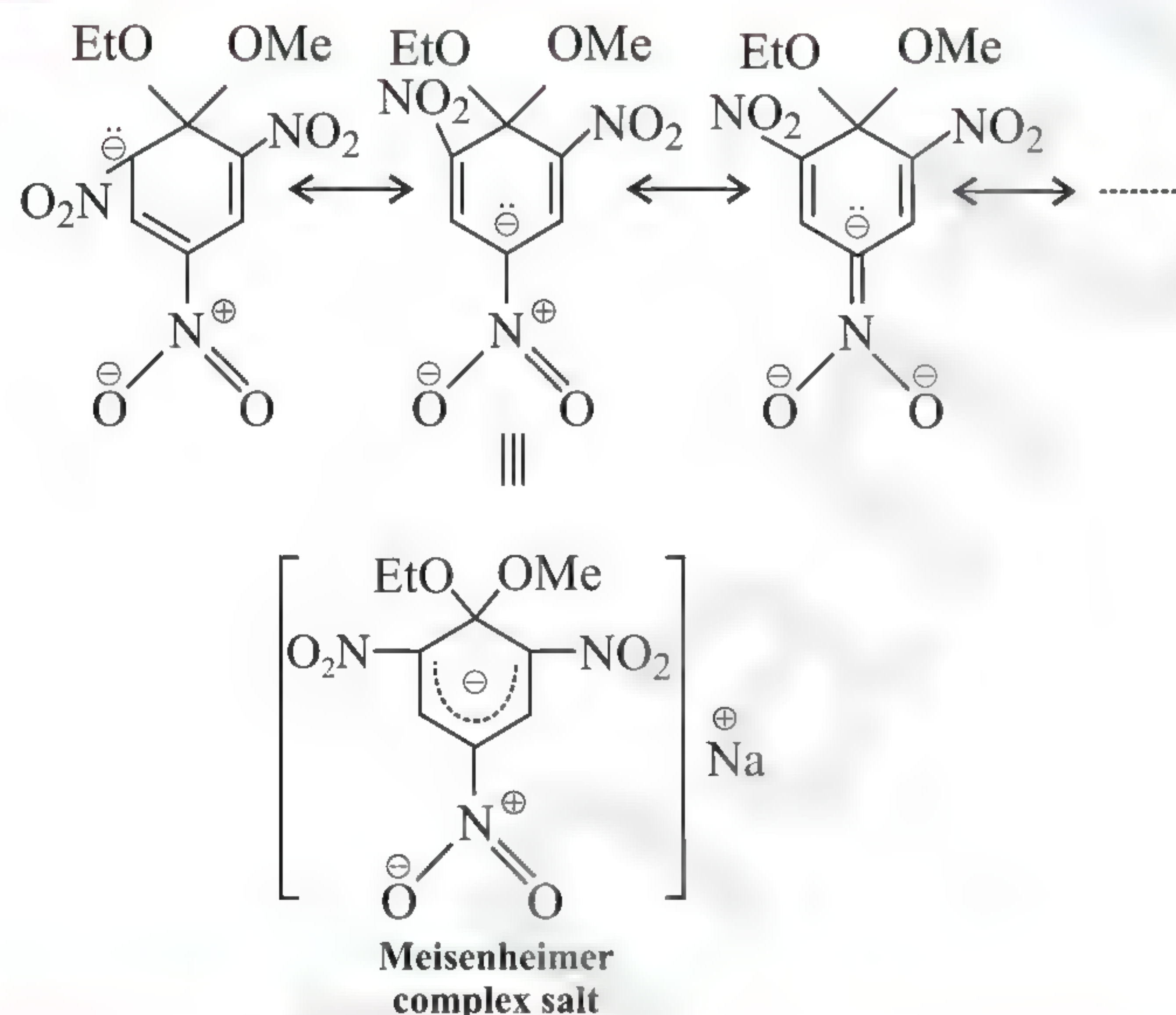
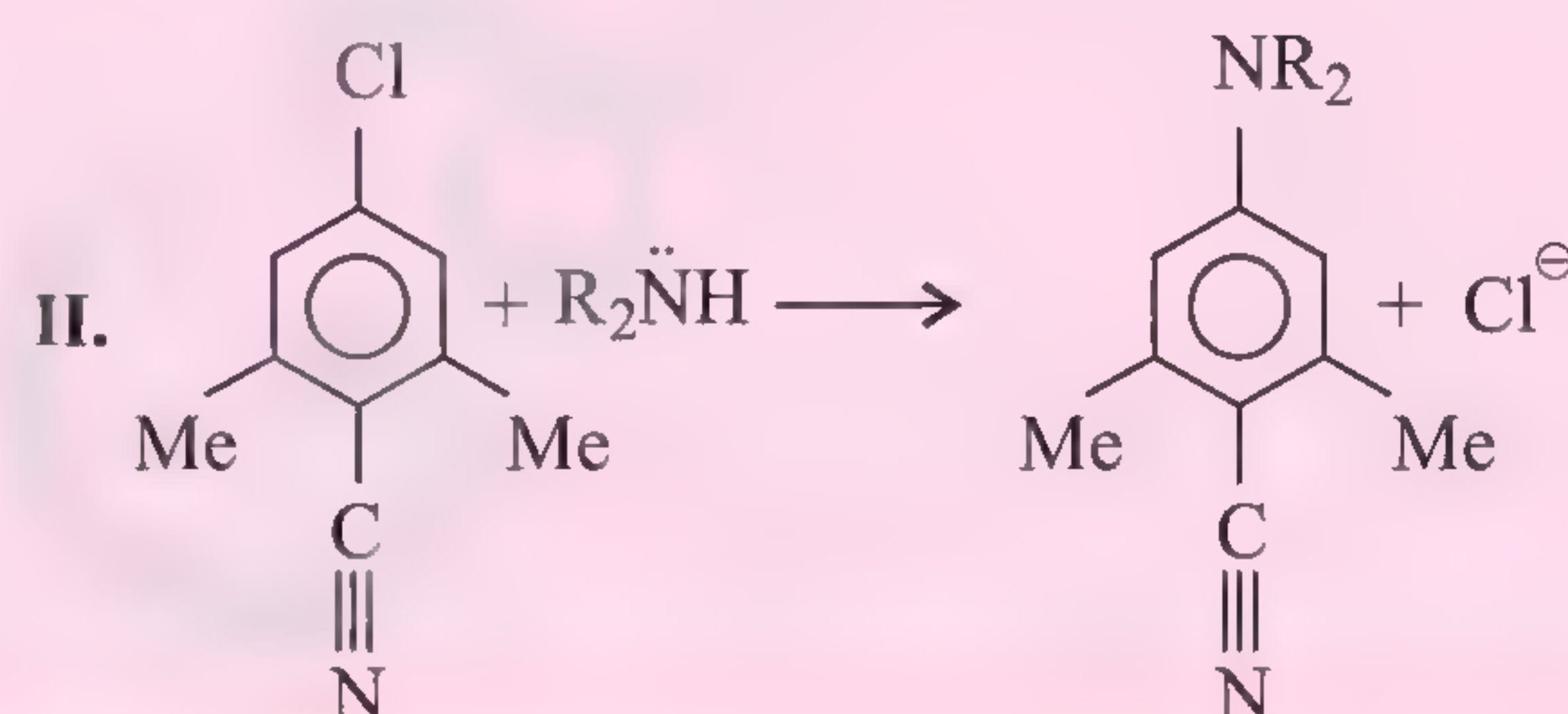
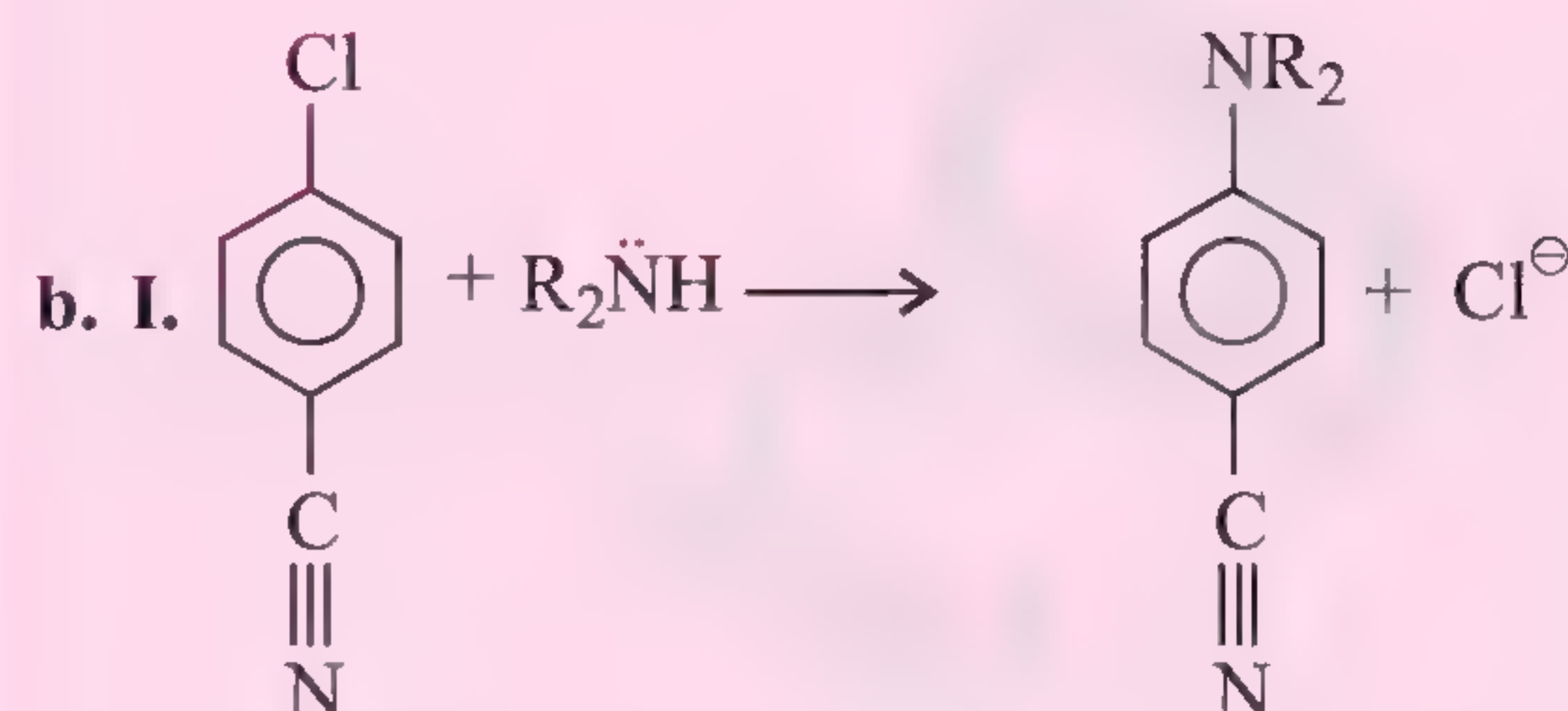
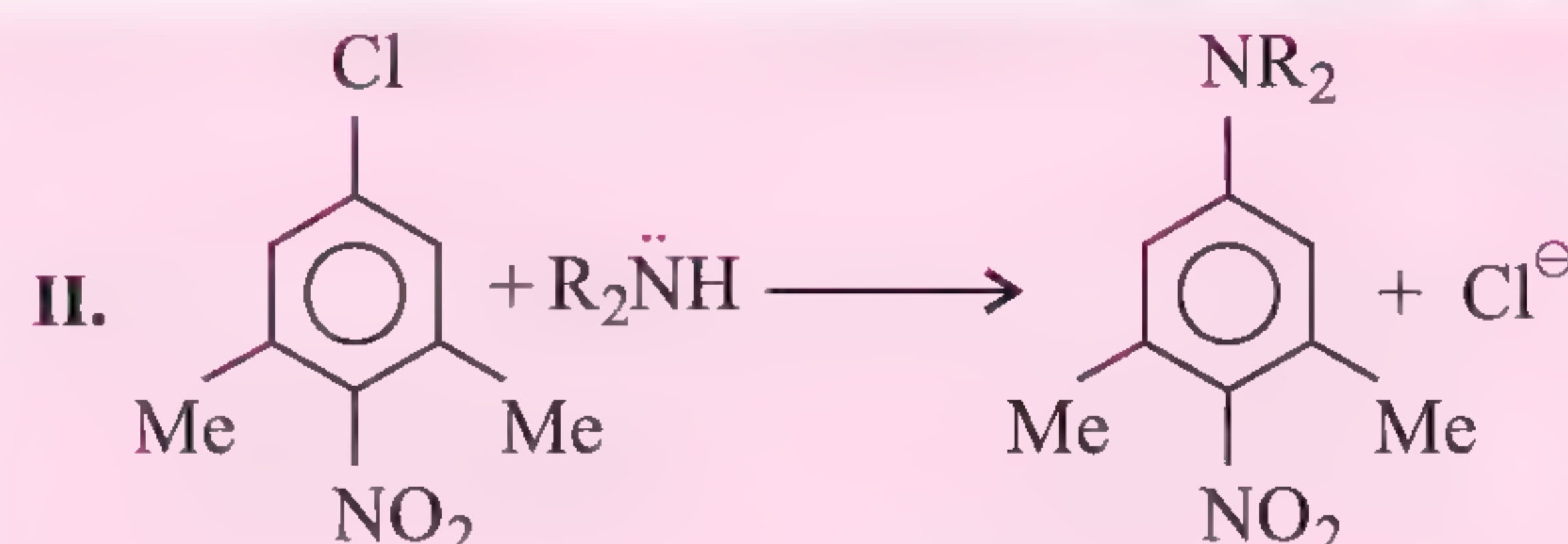
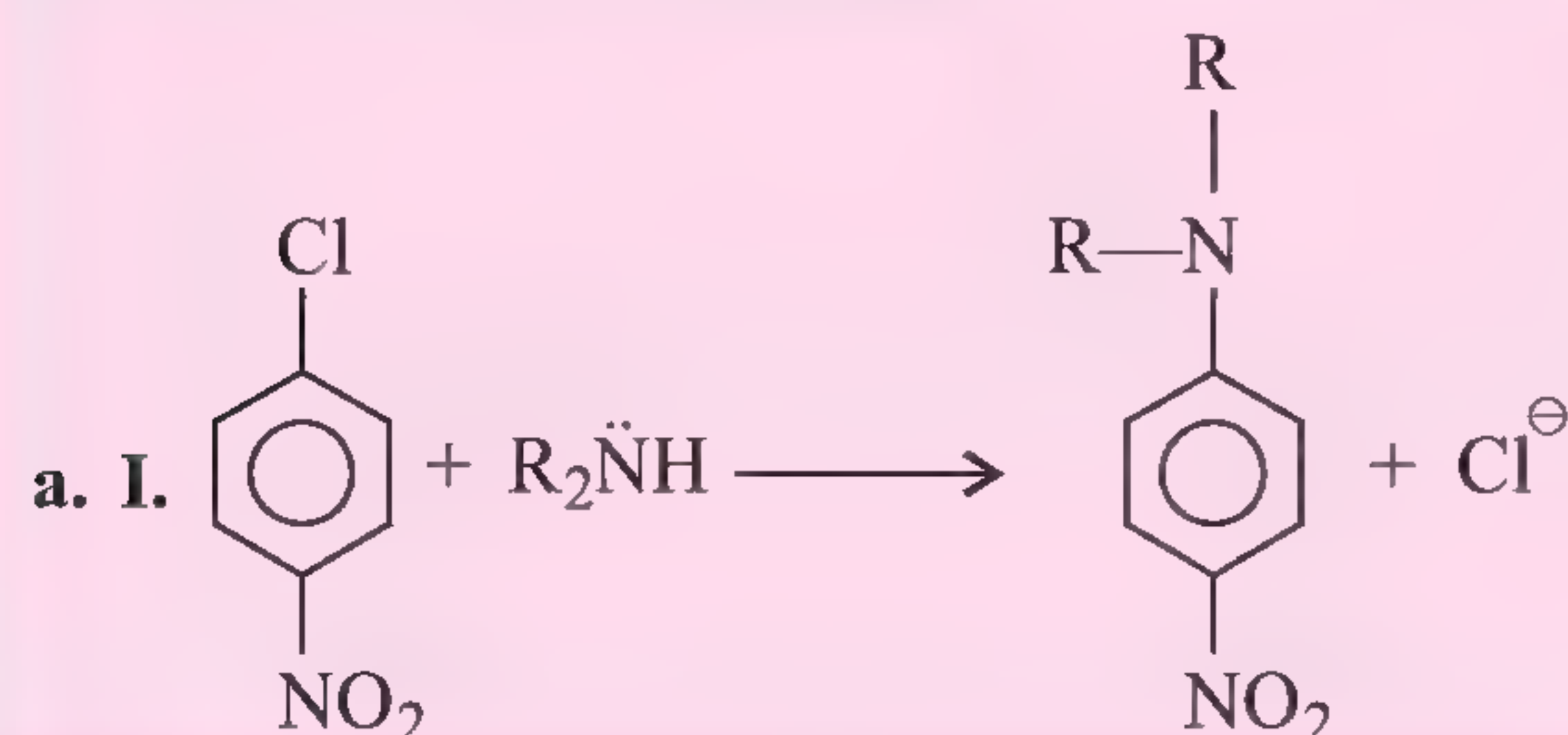


ILLUSTRATION 3.14

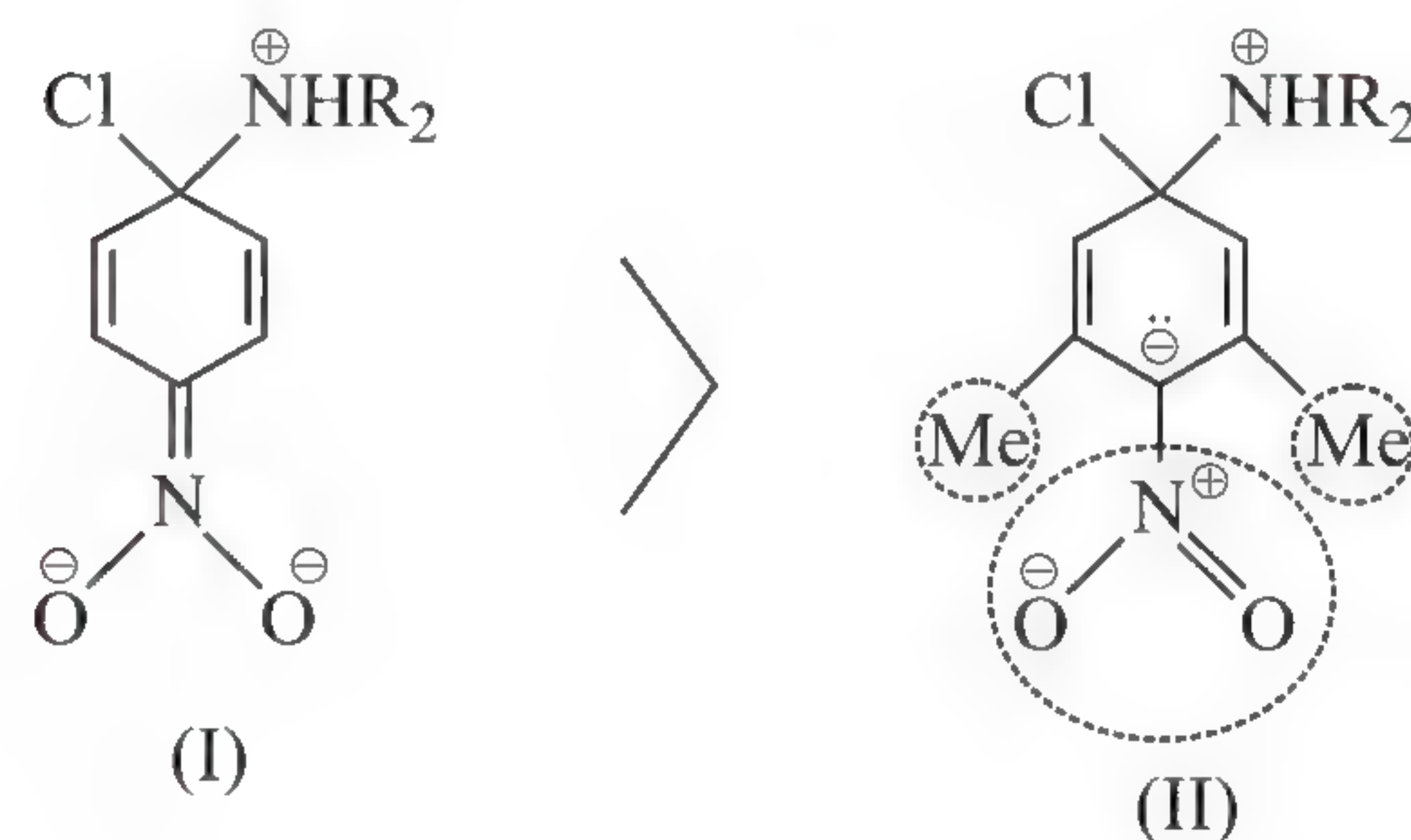
Give the decreasing order of reactivity of the following ArSN (addition-elimination reaction).



Sol.

a. Reactivity order: (I) > (II)

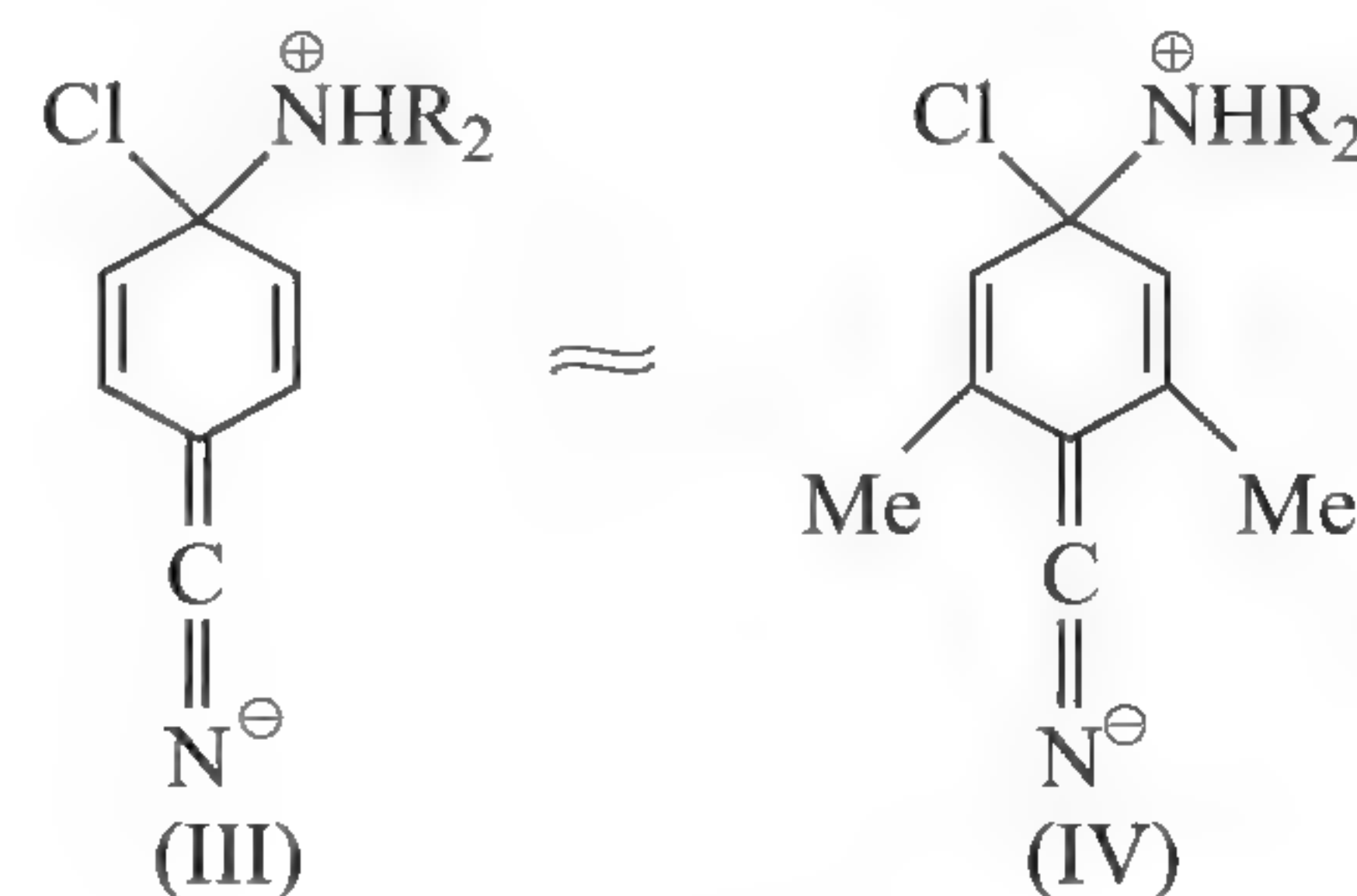
The intermediate T.S. of (I) and (II) are:



Coplanarity of ring with $(-\text{NO}_2)$ is disturbed due to steric inhibition of resonance

b. Reactivity order of (I) \approx (II)

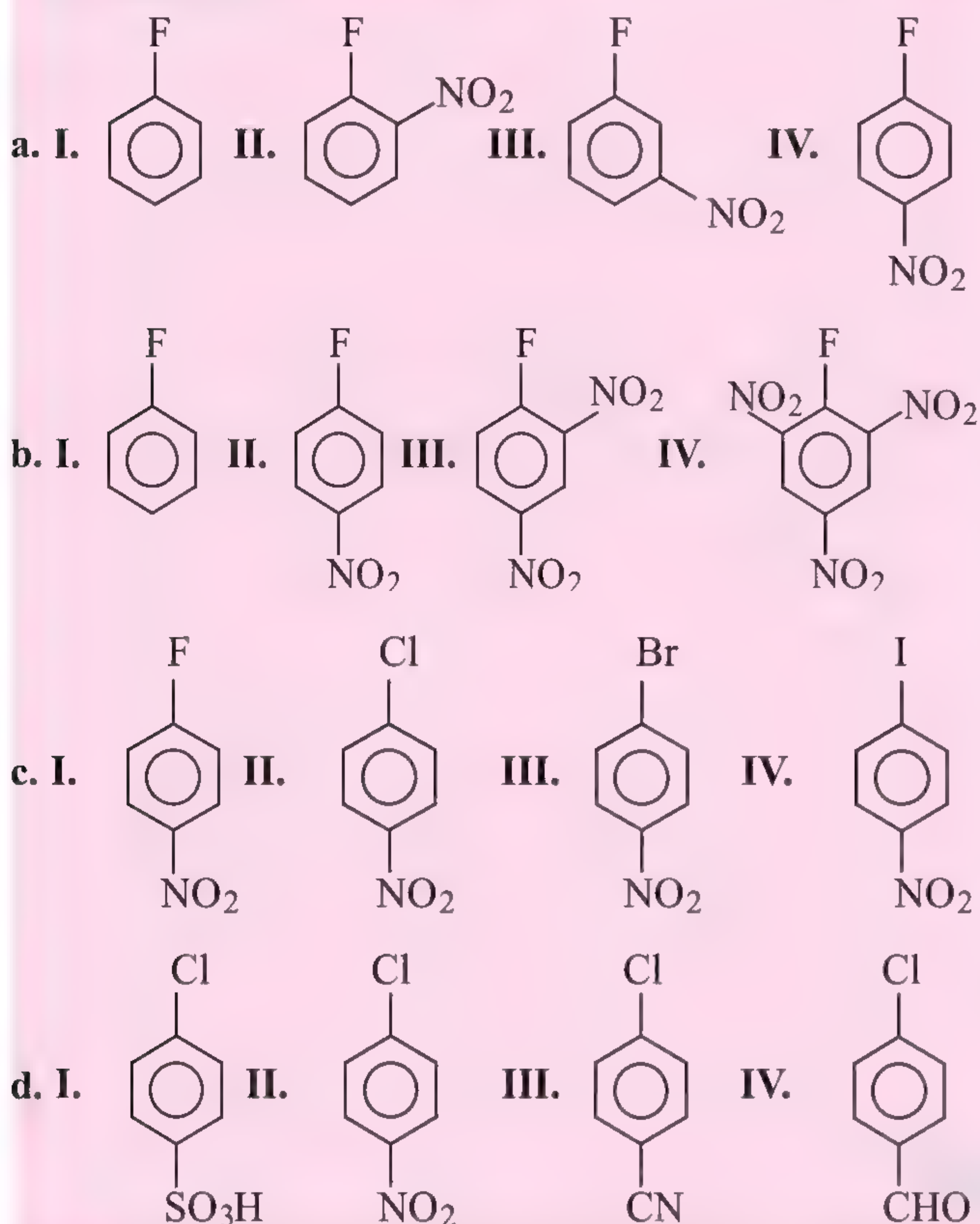
The intermediate TS of (I) and (II) is:



Since $(-\text{C}\equiv\text{N})$ group is linear, so coplanarity of the ring with $(-\text{C}\equiv\text{N})$ group is not disturbed; Resonance takes place

ILLUSTRATION 3.15

Give the decreasing order of ArSN reaction of the following with NaOMe:

**Sol.**

a. (II) > (IV) > (III) > (I).

The leaving group F is same, so the ArSN reactivity is determined by EWG ($-\text{NO}_2$) group. More the EWG, more rapid is the reaction. EW power of ($-\text{NO}_2$) at $o > p > m$. Although negative charge in arenanion is equally stabilised by ($-\text{NO}_2$) group at o - and p -position, $-I$ power of ($-\text{NO}_2$) group is slightly more at *ortho* than at *para*.

b. (IV) > (III) > (II) > (I)

More the number of EWG ($-\text{NO}_2$), faster is the ArSN reaction.

c. (I) > (II) > (III) > (IV) (See Illustration 3.24)

The leaving groups are different. More the EN of the leaving group, more is the negative charge stabilised in the intermediate arenanion, and hence faster is the reaction.

d. (II) > (I) > (III) > (IV)

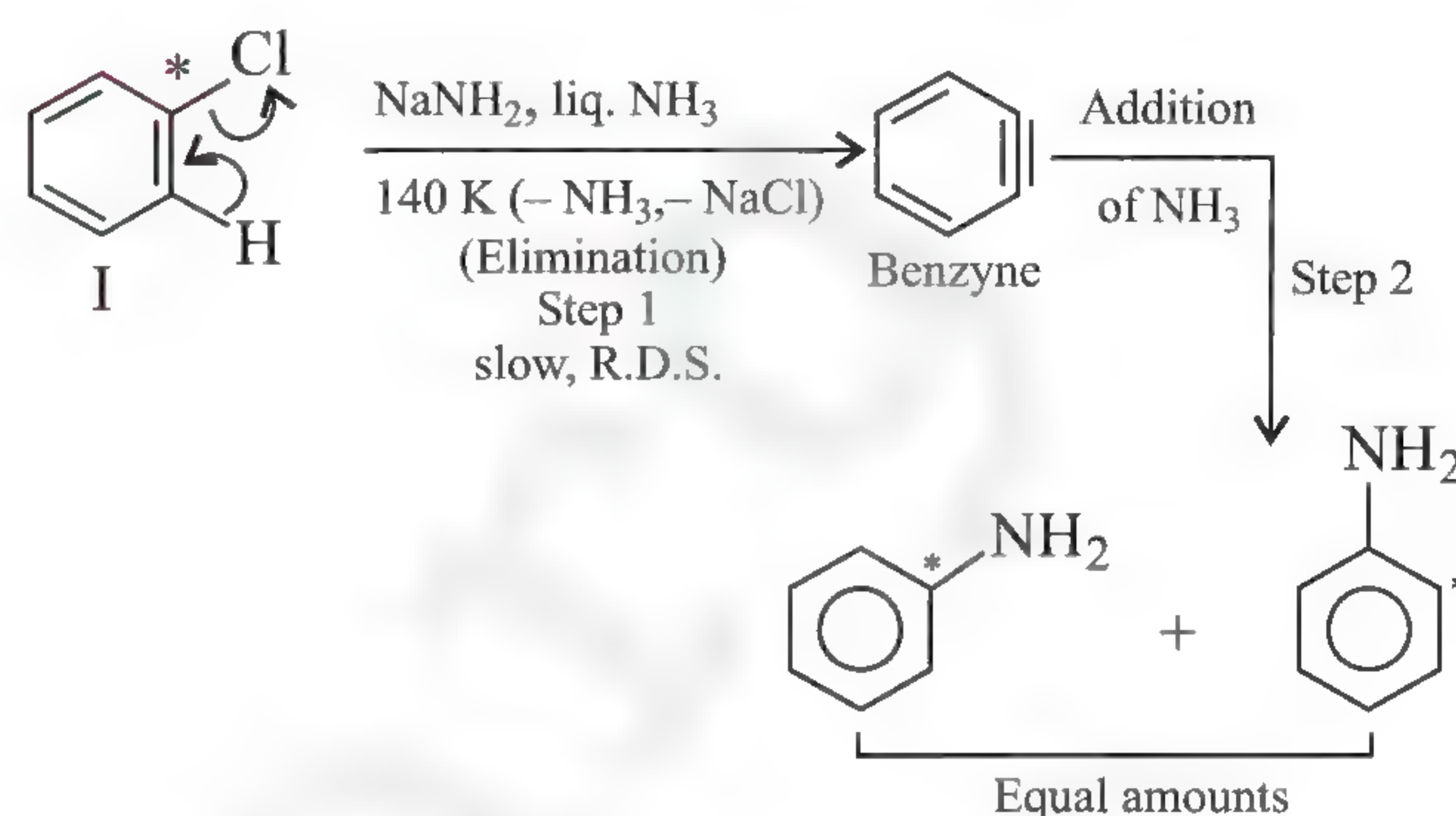
The leaving group Cl is same. ArSN reactivity is determined by EWG. More the EW power, more is the reactivity. The EW power of $-\text{NO}_2 > -\text{SO}_3\text{H} > -\text{C}\equiv\text{N} > -\text{CHO}$.

3.13 ArSN (ELIMINATION-ADDITION) REACTION VIA BENZYNE INTERMEDIATE

ArX undergoes nucleophilic substitution reaction in the presence of a very strong base such as NaNH_2 or KNH_2 in liquid NH_3 at -33°C (140 K). The reaction occurs through the formation of an intermediate called benzyne.

a. Two important features are:

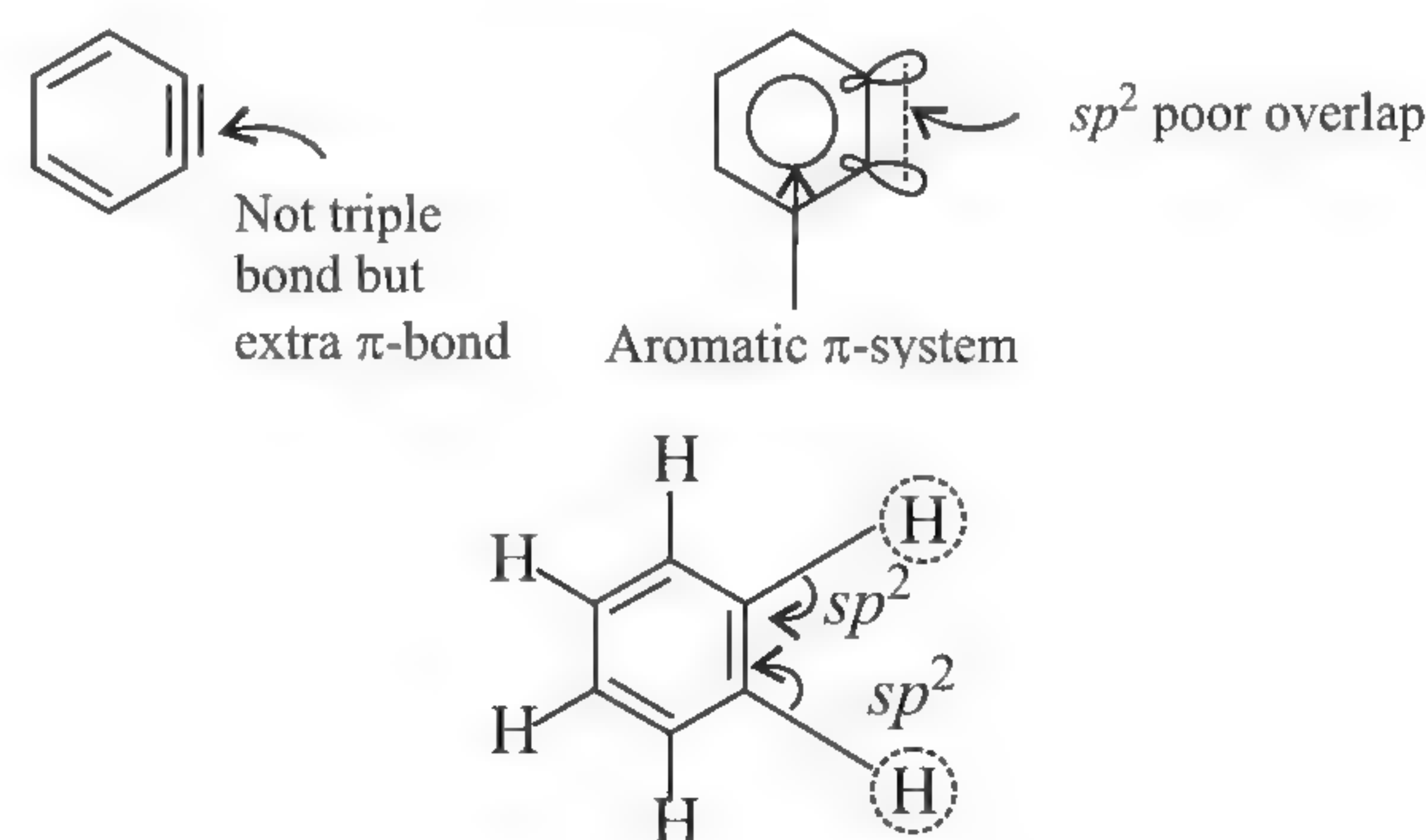
- There is no necessity of an \bar{e} -withdrawing group in the ArX.
- The entering group does not always occupy the vacated position. This is called **cine substitution**.



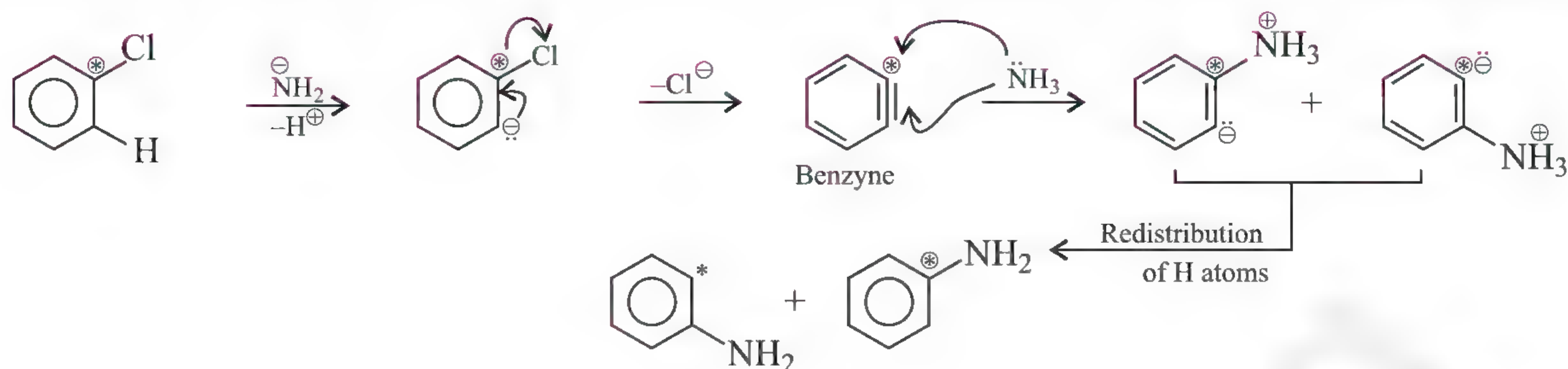
Step 1: Slow, R.D.S.

Since in this reaction first the elimination of HCl occurs and then the addition of NH_3 takes place, therefore this ArSN reaction is called elimination-addition reaction.

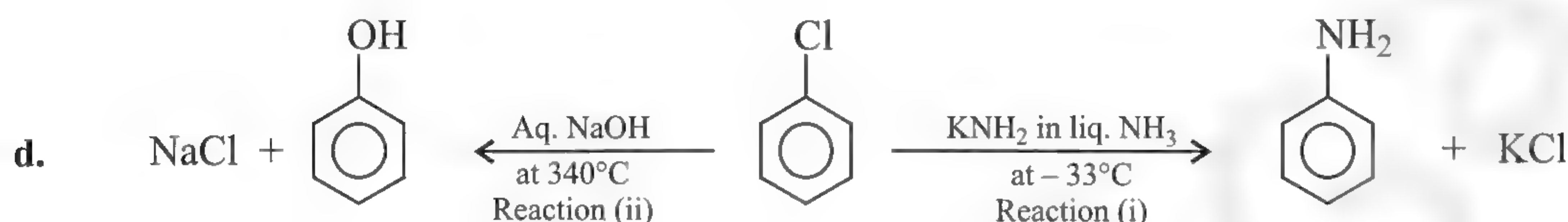
When chlorobenzene (I) with ^{14}C is treated with NaNH_2 in liquid NH_3 , half of the product has an ($-\text{NH}_2$) group attached to ^{14}C (C^*) as expected, but the other half has an ($-\text{NH}_2$) group attached to the carbon adjacent to ^{14}C (C^*). This observation proves the formation of a benzyne intermediate which has two equivalent C atoms to which the ($-\text{NH}_2$) group can be attached. Benzyne has an additional π -bond formed by sideways overlap of sp^2 orbitals alongside the ring. These orbitals that form π -bond cannot overlap with the aromatic π -system because they are not coplanar. The new π -bond is weak because of the poor overlap and hence benzyne is very reactive.



- b. **Mechanism:** The strong base (NH_2^-) removes the H^+ to give a high-energy carbanion which removes the X^- to give a triply bonded intermediate called a benzyne (elimination). The nucleophilic solvent adds to the reactive benzyne (addition) giving the final product after redistribution of H atoms.



c. **Existence of benzyne:** It is proved by trapping benzyne in Diels–Alder reaction.



Both the reactions are elimination–addition reactions and proceed *via* benzyne intermediate. Very strong base (NH_2^-) in reaction (i) and high temperature in reaction (ii) favours the reaction.

e. **Dow's process:** For the manufacture of phenol, chlorobenzene is fused with NaOH at elevated temperature and pressure. ArSN of PhCl by OH^- under drastic conditions takes place *via* benzyne intermediate to give phenol and other products.

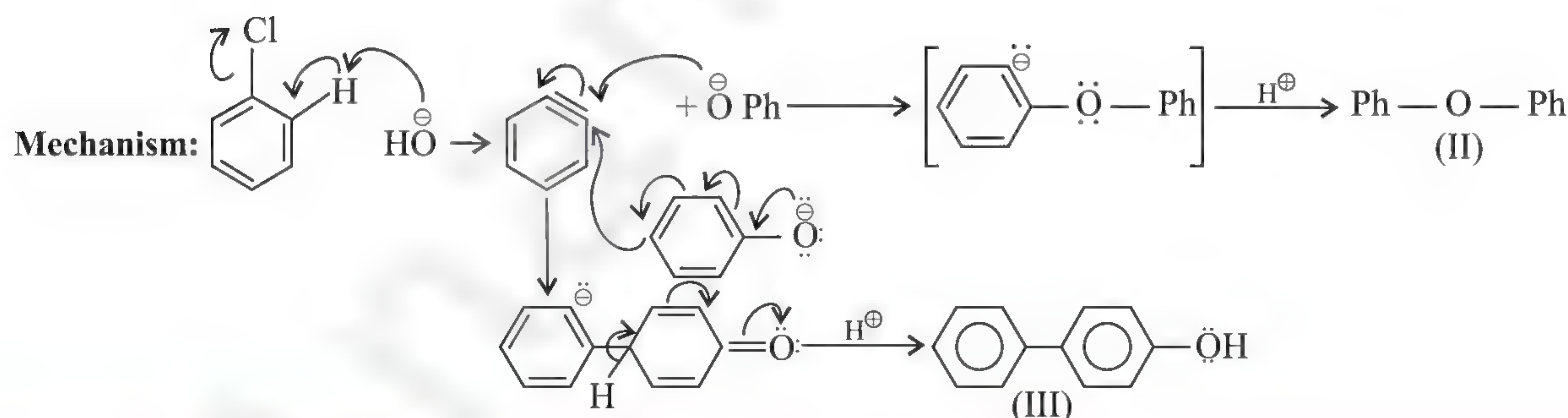
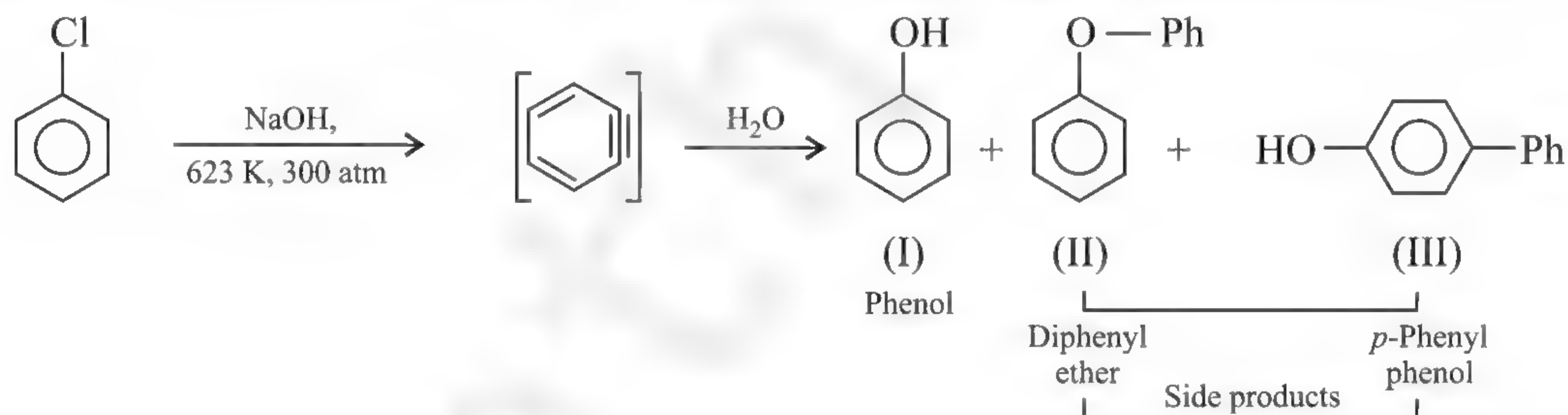
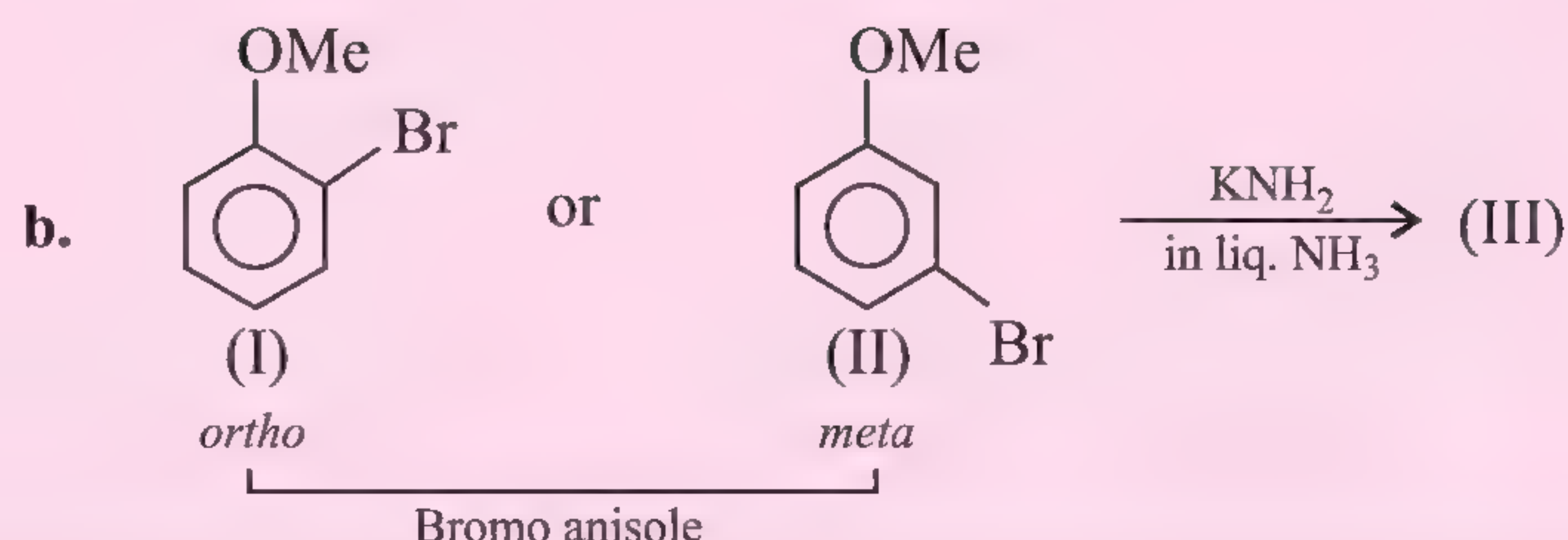
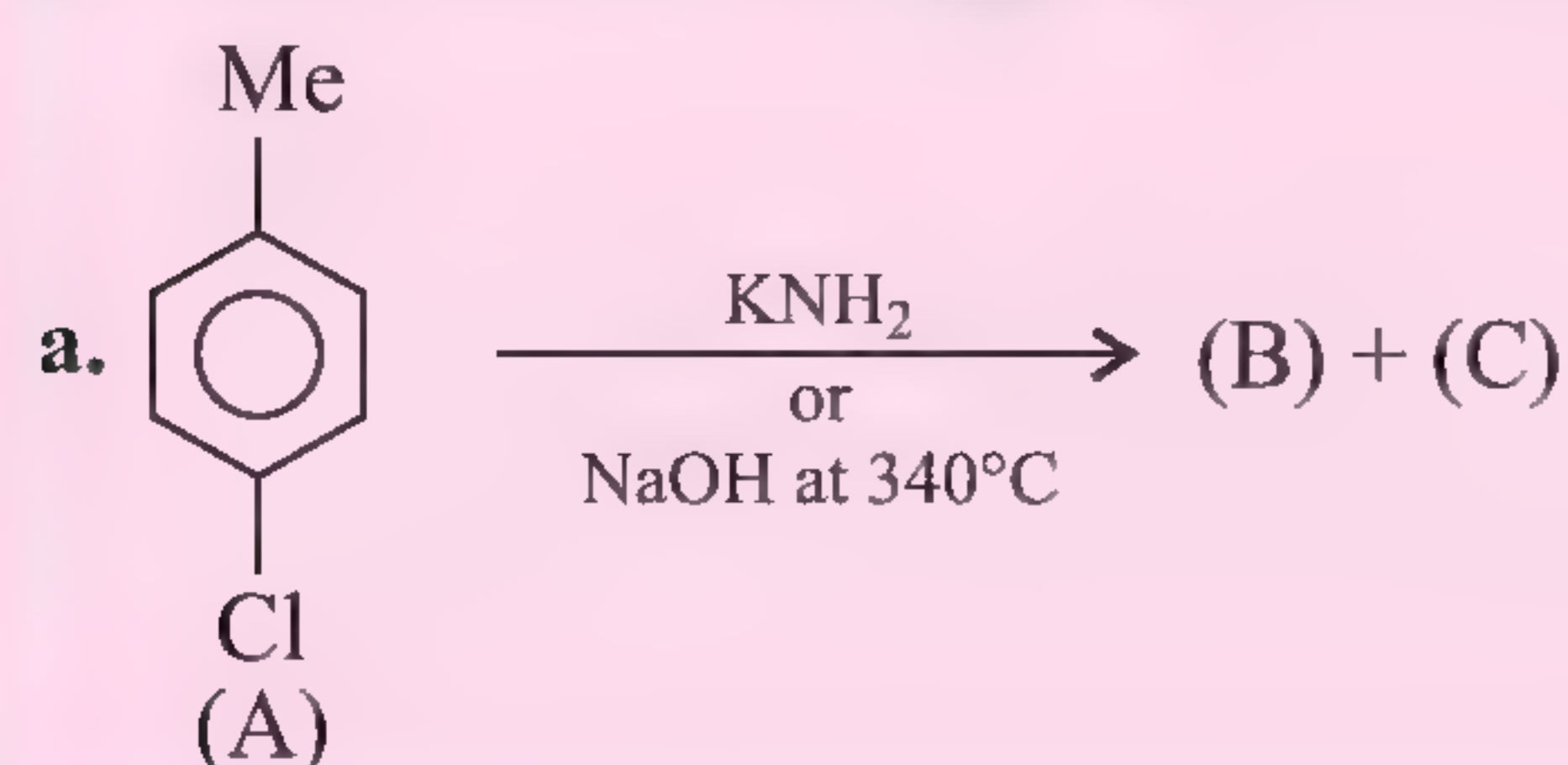
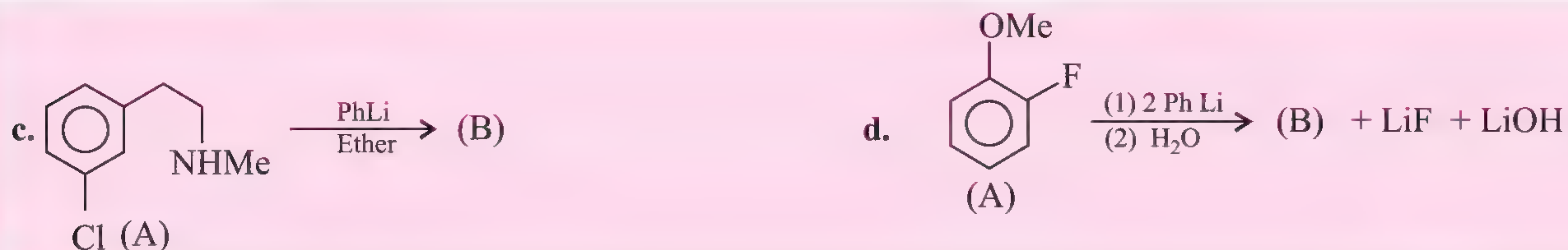


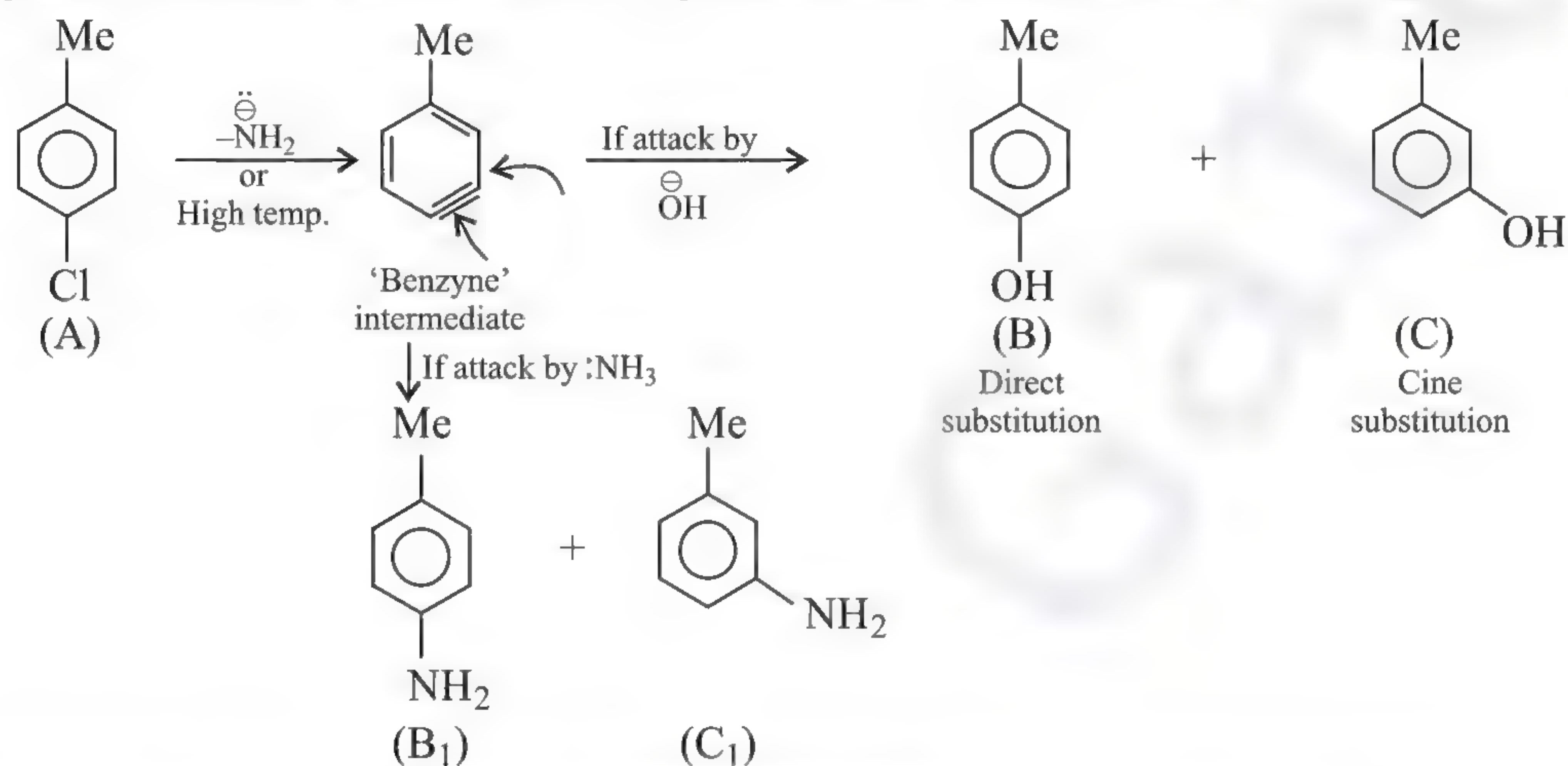
ILLUSTRATION 3.16

Give the reaction and explain the formation of the products.

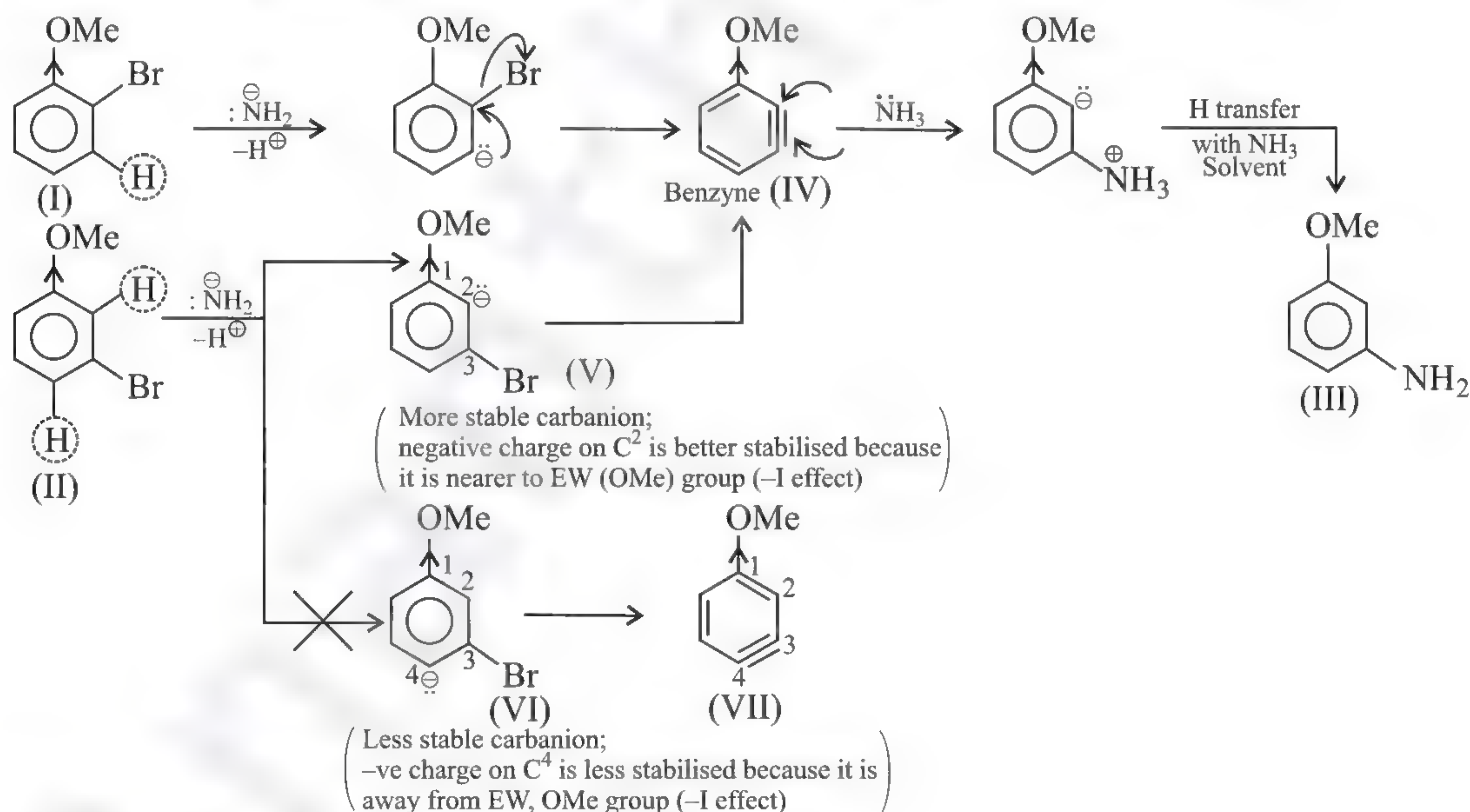


**Sol.**

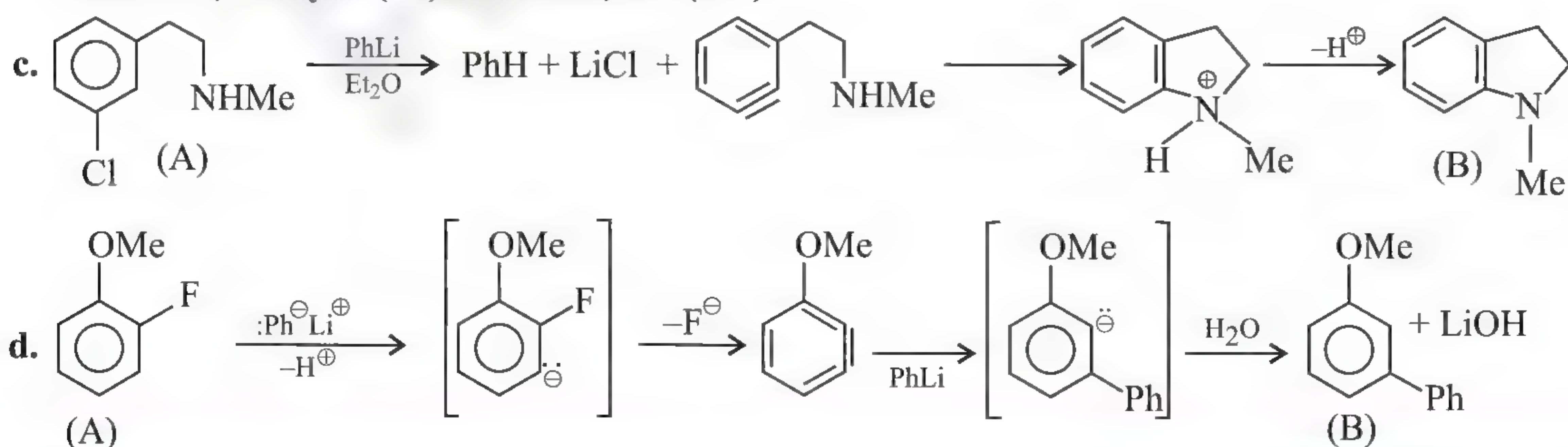
- a. With strong base such as NH_2^- or with OH^- at 340°C , the formation of benzyne intermediate is favoured, giving direct substitution product (B or B_1) and cine substitution product (C or C_1) (when the entering group does not occupy the vacated position).



- b. Both the isomers *o*- and *m*- [(I) and (II)] react by benzyne intermediate to give *m*-bromo anisole (III).

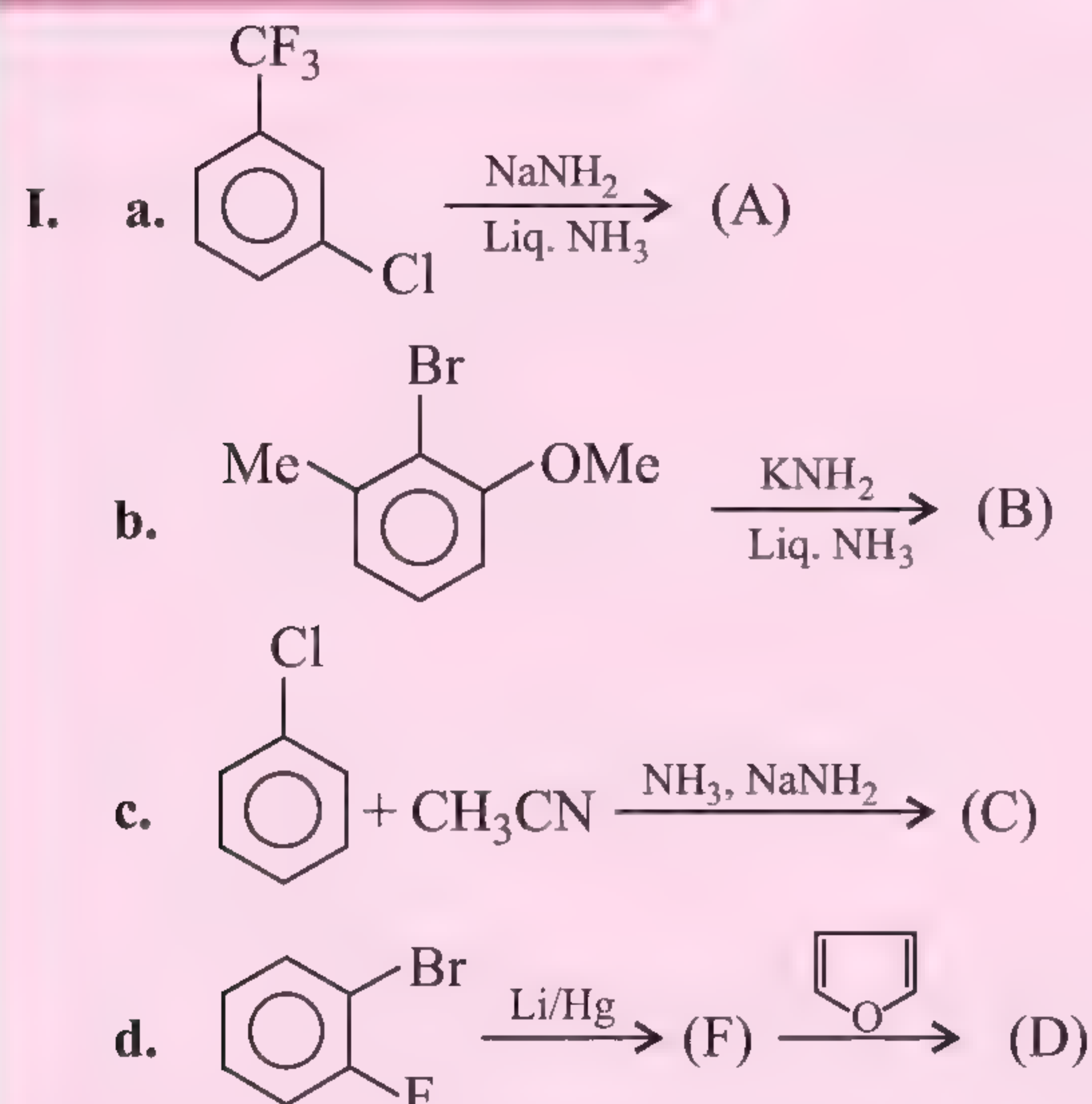


Therefore, benzyne (IV) is formed, not (VII).



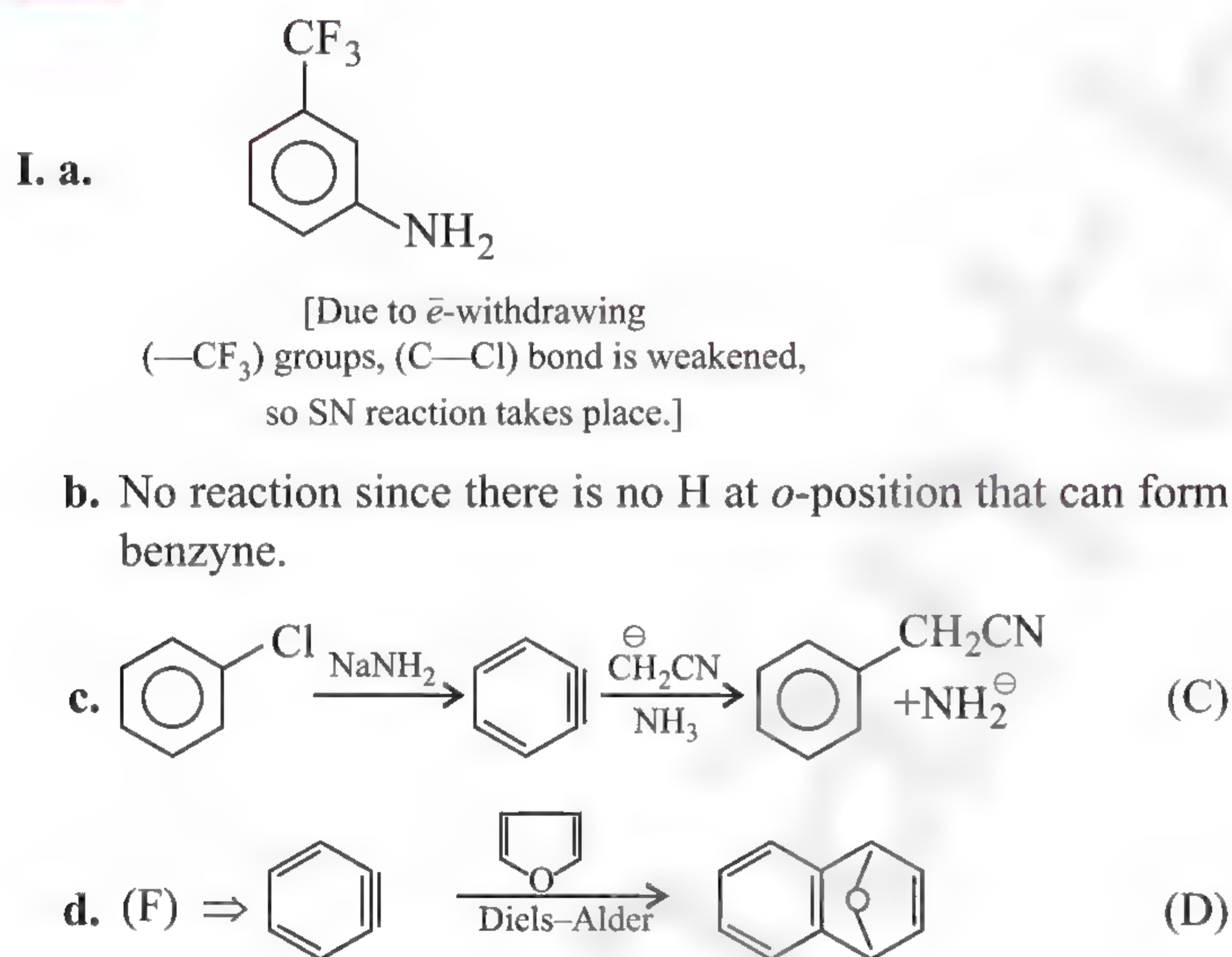
Note: Ph^- adds at *m*-position inducing the negative charge ortho to the \bar{e} -withdrawing ($-\text{OMe}$) group ($-I$ effect.)

ILLUSTRATION 3.17



II. When a trace of KNH_2 is added to a solution of chlorobenzene and potassium triphenyl methide ($\text{Ph}_3\text{C}^-\text{K}^+$) in liquid NH_3 , a rapid reaction takes place to yield a product of formula $\text{C}_{25}\text{H}_{20}$. What is the product? What is the role of KNH_2 and why is it needed?

Sol.



II. $\text{C}_{25}\text{H}_{20}$ suggests that the product is tetraphenyl methane Ph_4C . KNH_2 is used to produce benzyne which combines with $\text{Ph}_3\text{C}^-\text{K}^+$ to give the final product.

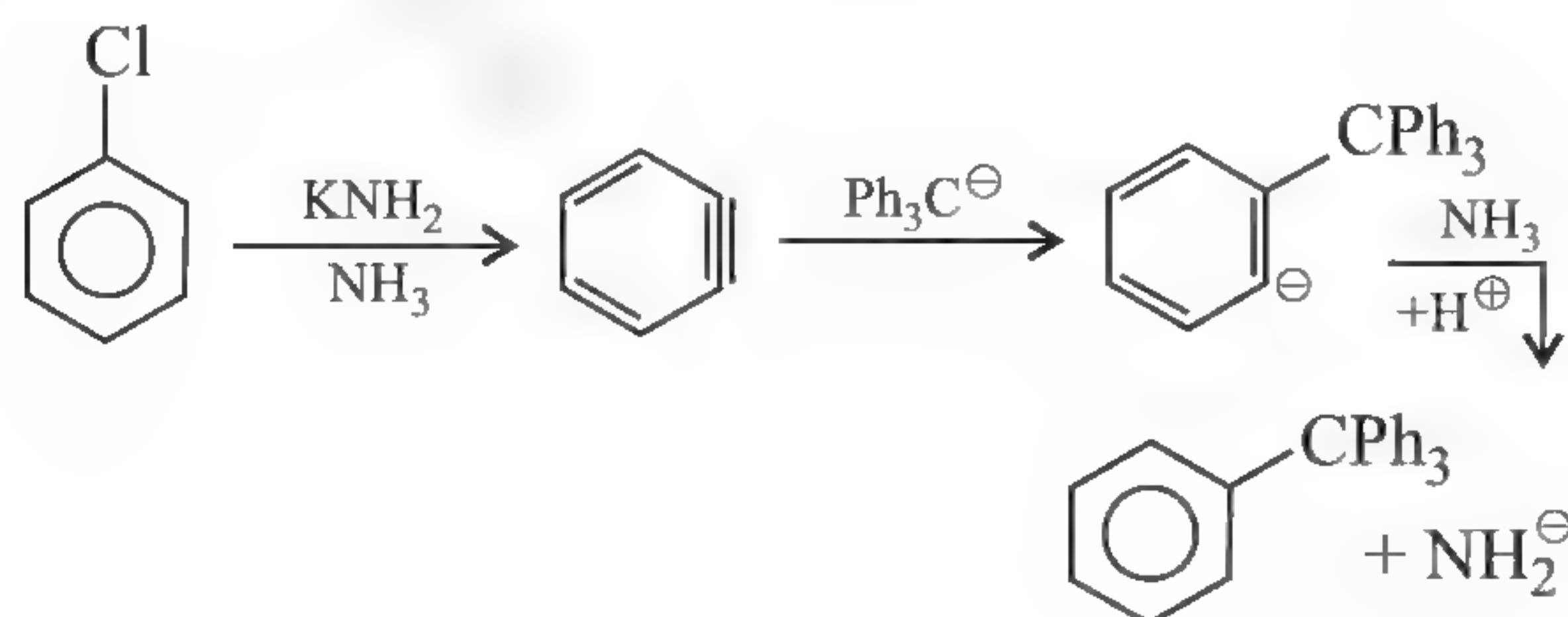
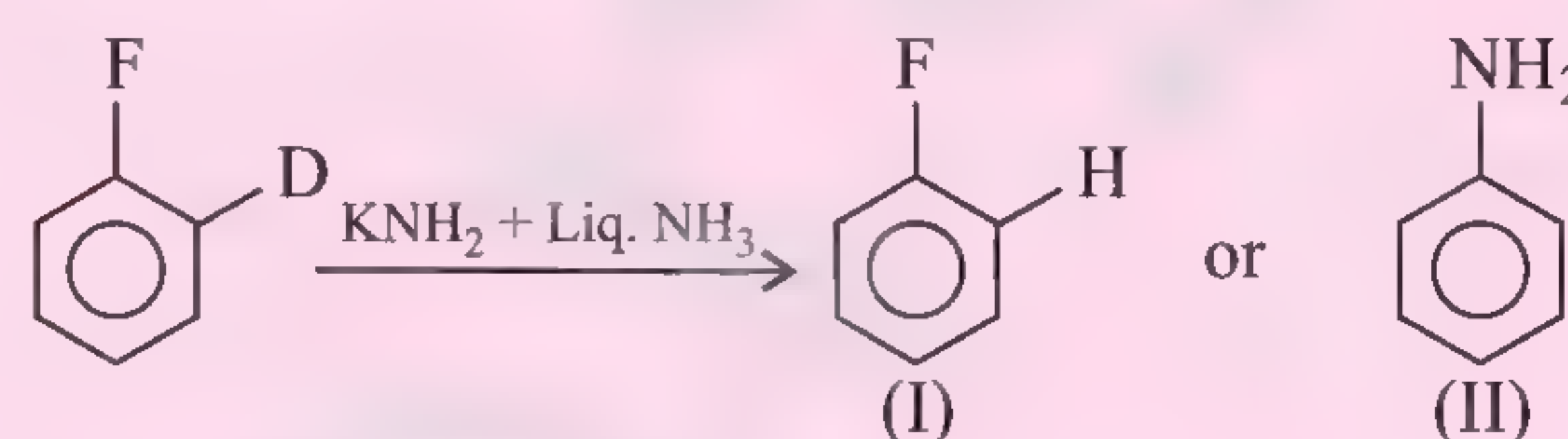


ILLUSTRATION 3.18

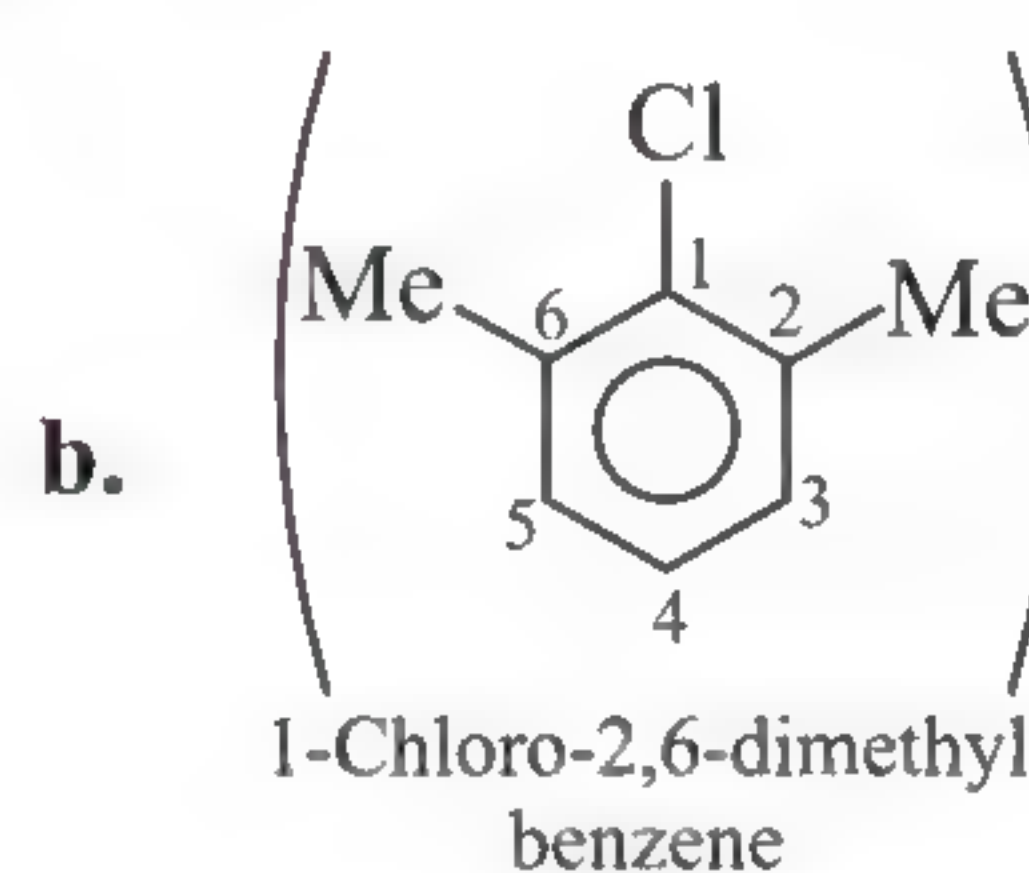
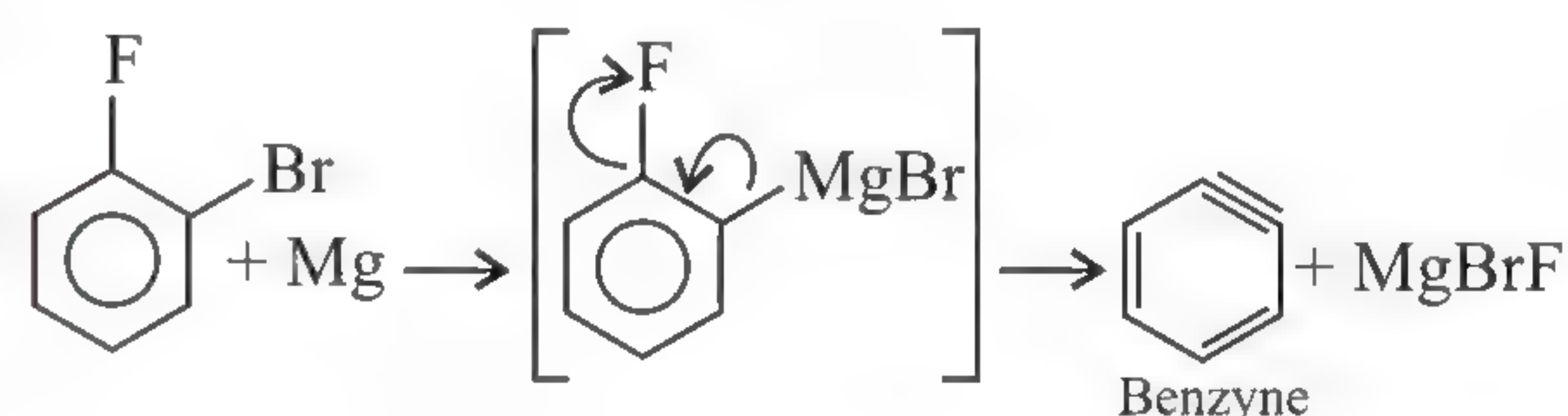
- Show that reaction of *o*-bromofluorobenzene with Mg produces benzyne.
- Why does 1-chloro-2,6-dimethyl benzene not undergo elimination–addition reaction with NaNH_2 in liq. NH_3 ?
- Why does bromobenzene react faster than 2,6-dideuterio-bromobenzene with NaNH_2 in liq. NH_3 ?
- In the following reactions:



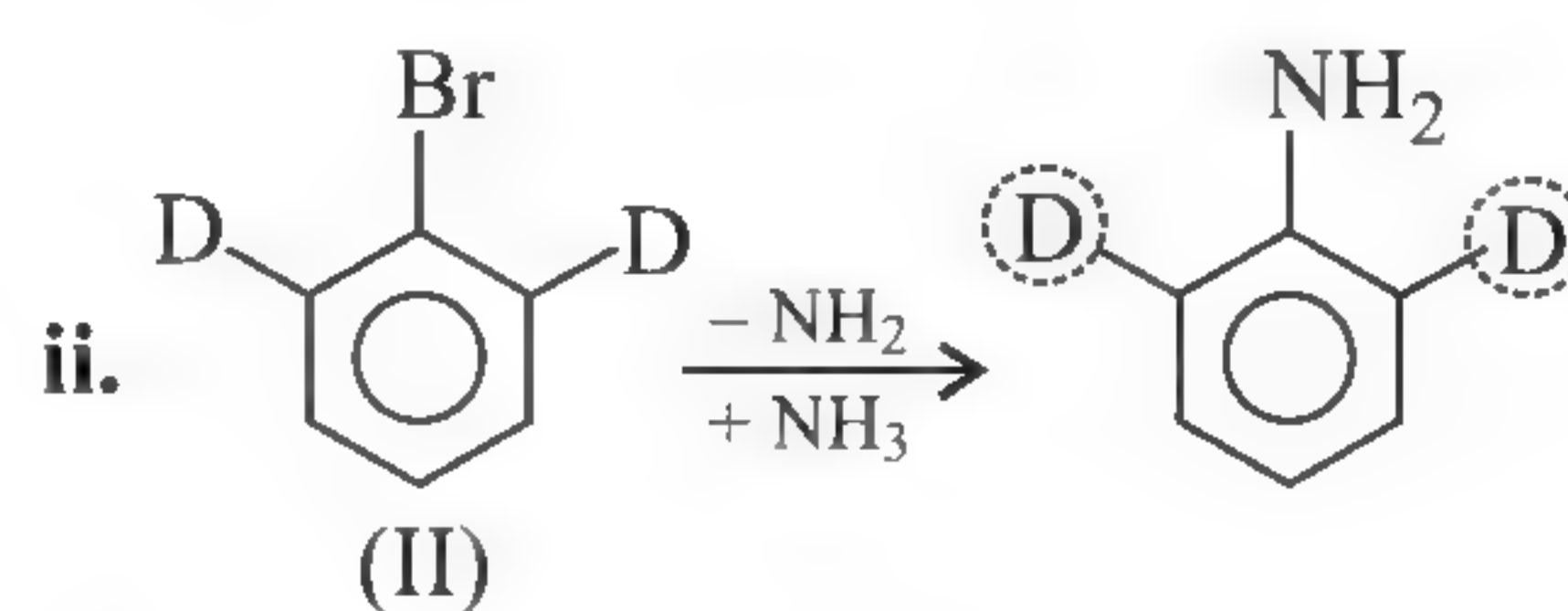
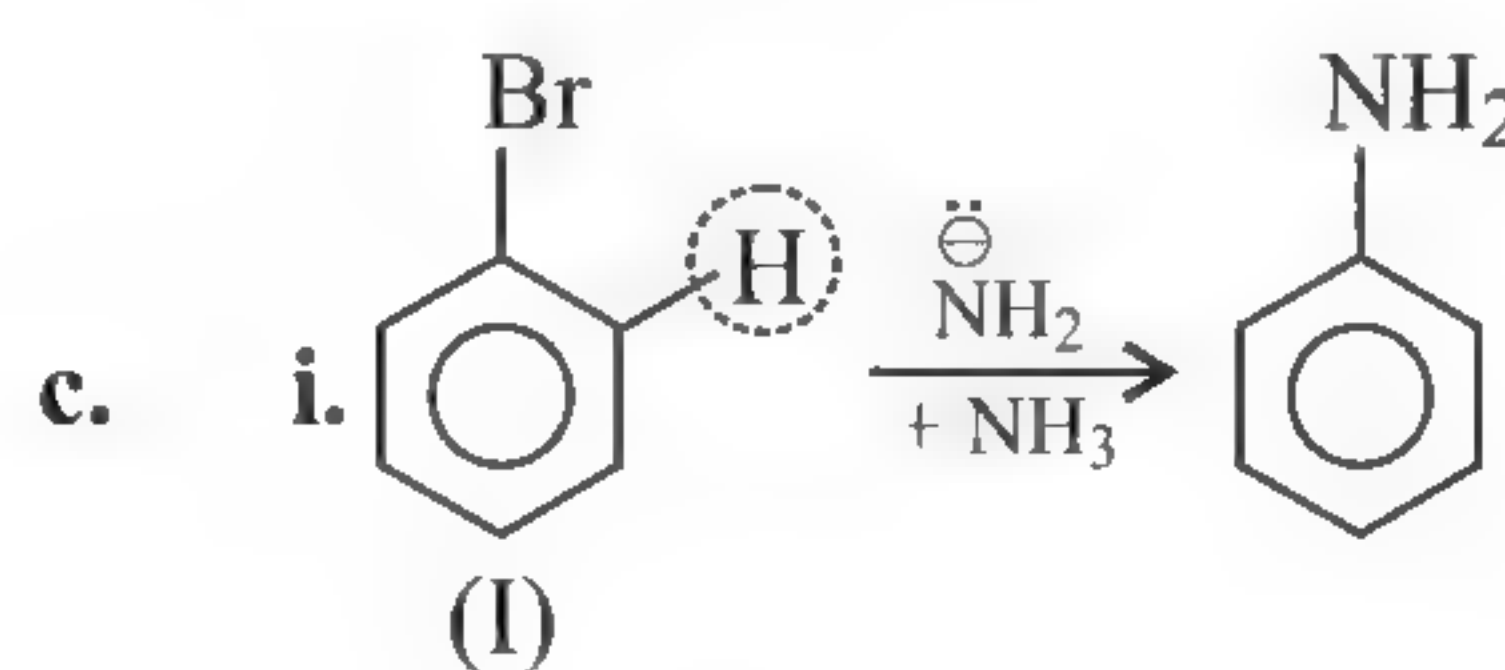
Explain why the formation of (I) is faster than that of (II).

Sol.

- Mg forms the Grignard reagent with Br and then carbanion removes F^- . G.R. is formed with Br not with F due to weak (C—Br) bond.



It does not form benzyne intermediate because there is no *ortho* H atom.



Reaction (i) is faster than (ii), since (C—H) bond is weaker than (C—D) bond, and therefore (C—H) bond is broken

faster in the first rate-determining step. There is possibility of E2-type mechanism in which the formation of extra π -bond resulting from breaking of (C—H) bond and leaving of X takes place simultaneously.

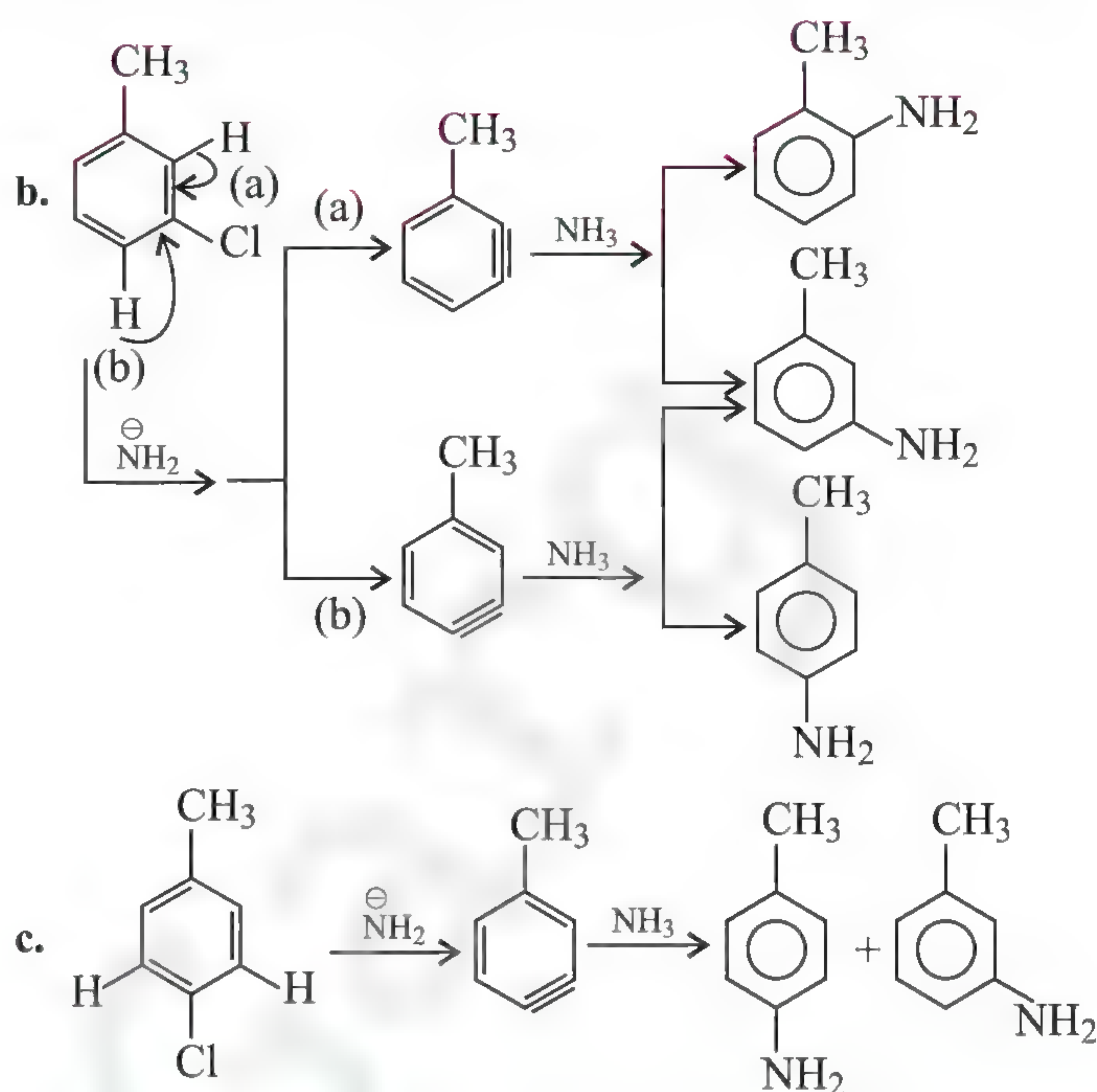
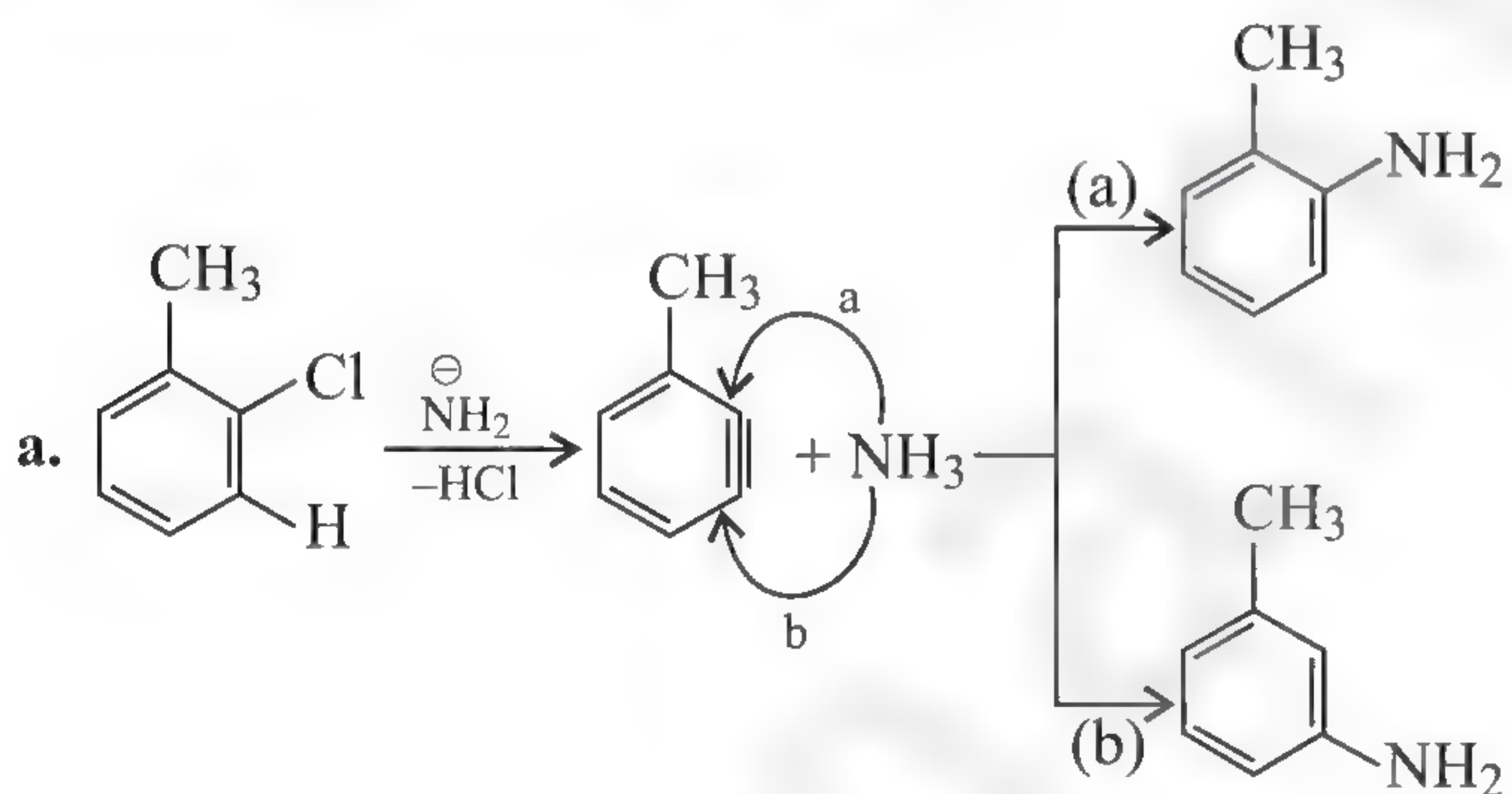
- d. Exchange of H from solvent (NH_3) to the intermediate anion $\left(\text{C}_6\text{H}_5\text{F}^-\right)$ is faster than breaking of the (C—F) bond to form benzyne because the (C—F) bond is very strong. D/H exchange eliminates the possibility of E2-type mechanism.

ILLUSTRATION 3.19

When three isomeric chlorotoluenes are treated with KNH_2 in liquid NH_3 , they yield different toluidines as shown below. Explain these observations.

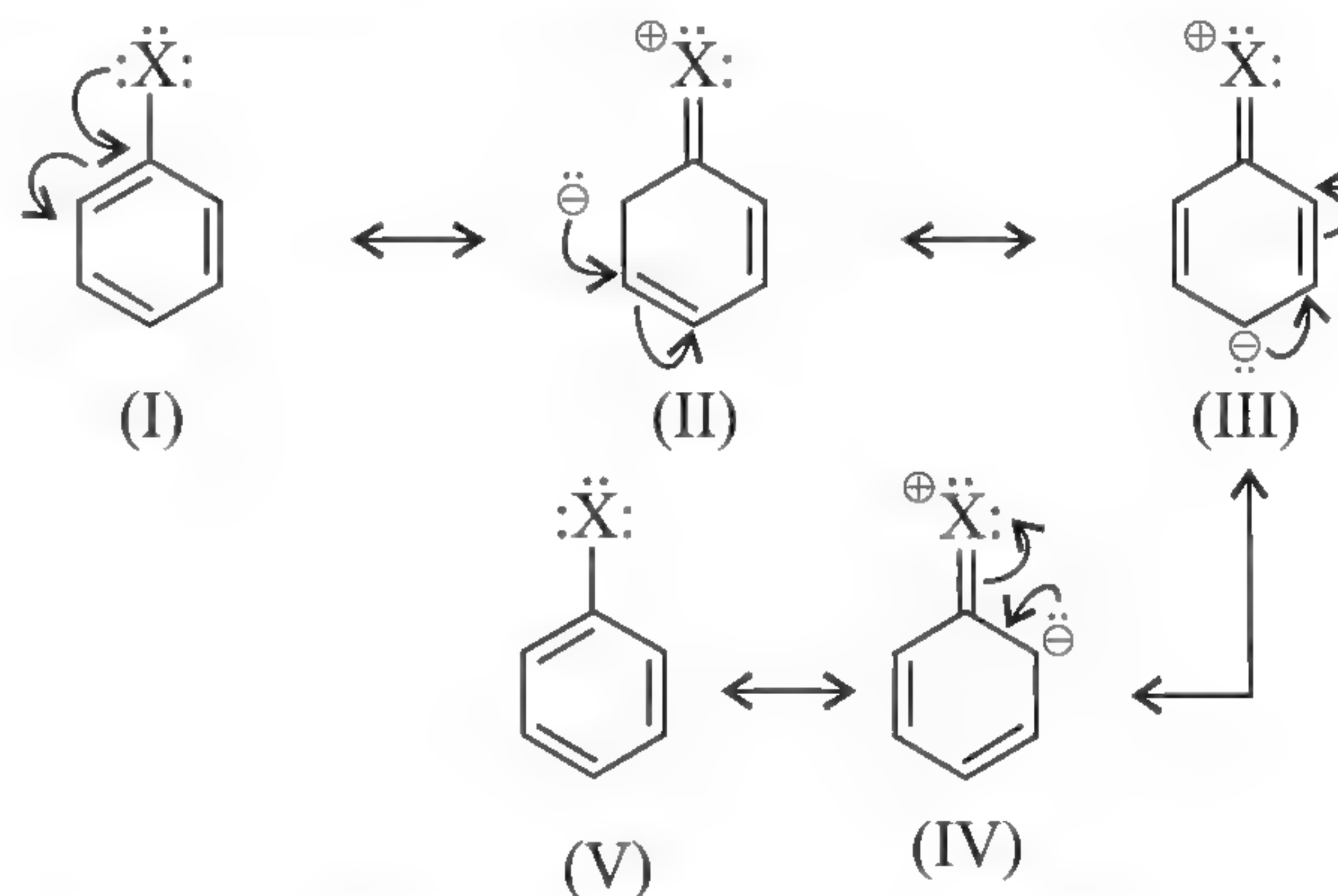
- o*-Chlorotoluene \longrightarrow (*o* + *m*)-Toluidine
- m*-Chlorotoluene \longrightarrow (*o* + *m* + *p*)-Toluidine
- p*-Chlorotoluene \longrightarrow (*m* + *p*)-Toluidine

Sol. The reaction involves aryne intermediates. In *o*-chlorotoluene, only one *o*-hydrogen is available and so its elimination generates only one aryne, whereas the availability of two *o*-hydrogens in *m*-chlorotoluene generates two arynes. Although two *o*-hydrogens are available in *p*-chlorotoluene, their elimination generates only one aryne.

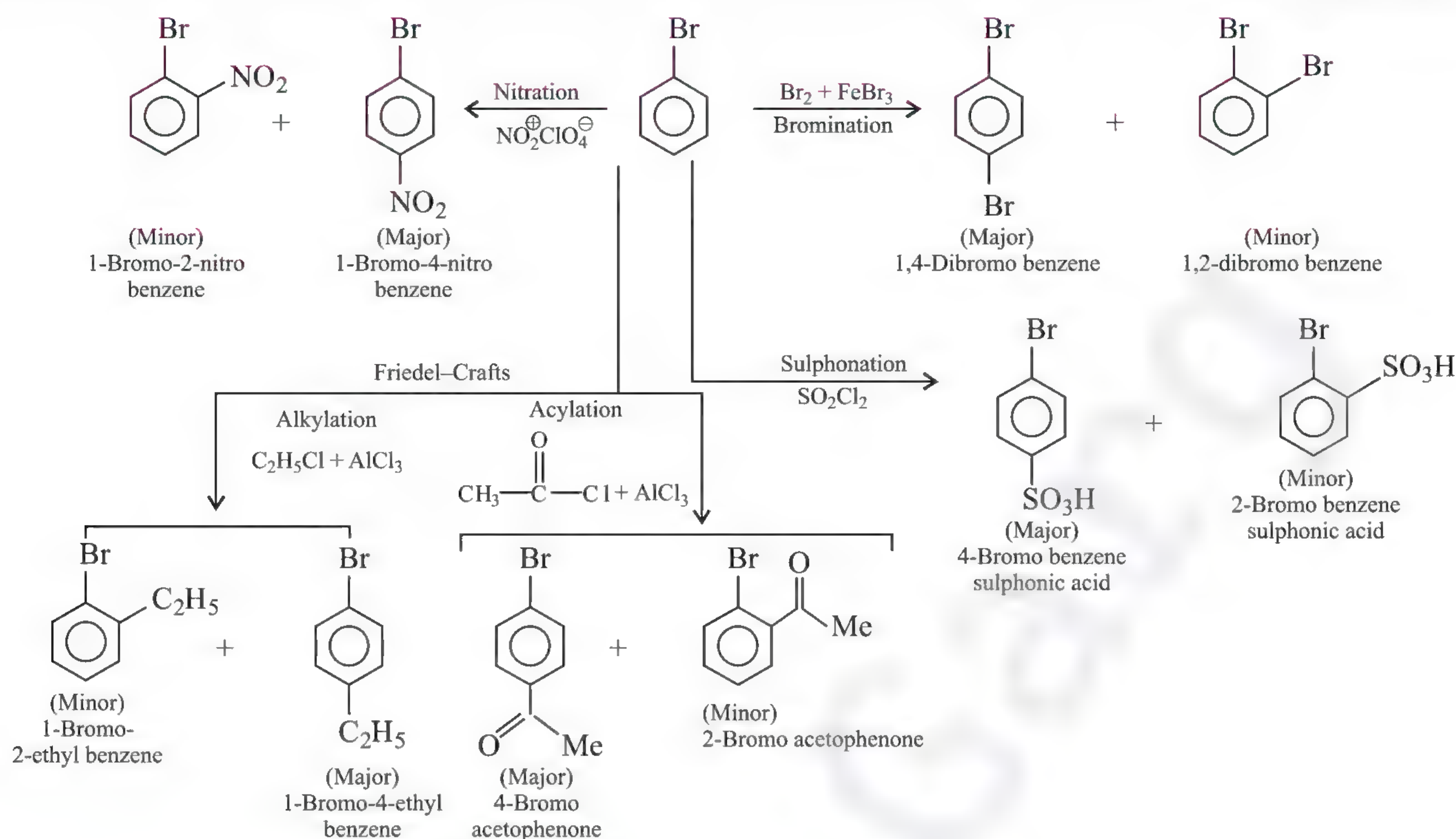


3.14 SE REACTIONS OF ARYL HALIDES

ArX undergoes the usual SE reactions of the benzene ring such as halogenation, sulphonation, nitration, and Friedel–Crafts reactions. Although slightly deactivating (due to $-\text{I}$ effect), yet they are *o*, *p*-directing. Orientation (*o*-, *p*-directing) influence of halogens is explained by the resonance. Due to $+\text{R}$ effect, ArX is resonance stabilised as follows:



Due to resonance, benzene ring is activated at *o*- and *p*-positions, thereby increasing the \bar{e} density more at *o*- and *p*-positions than at *m*-positions. Moreover, due to $-\text{I}$ effect of X, there is some tendency to withdraw \bar{e} 's from the benzene ring; as a result, the ring gets slightly deactivated as compared to benzene and hence SE reaction in ArX occurs slowly and drastic conditions are required as compared to those in benzene.



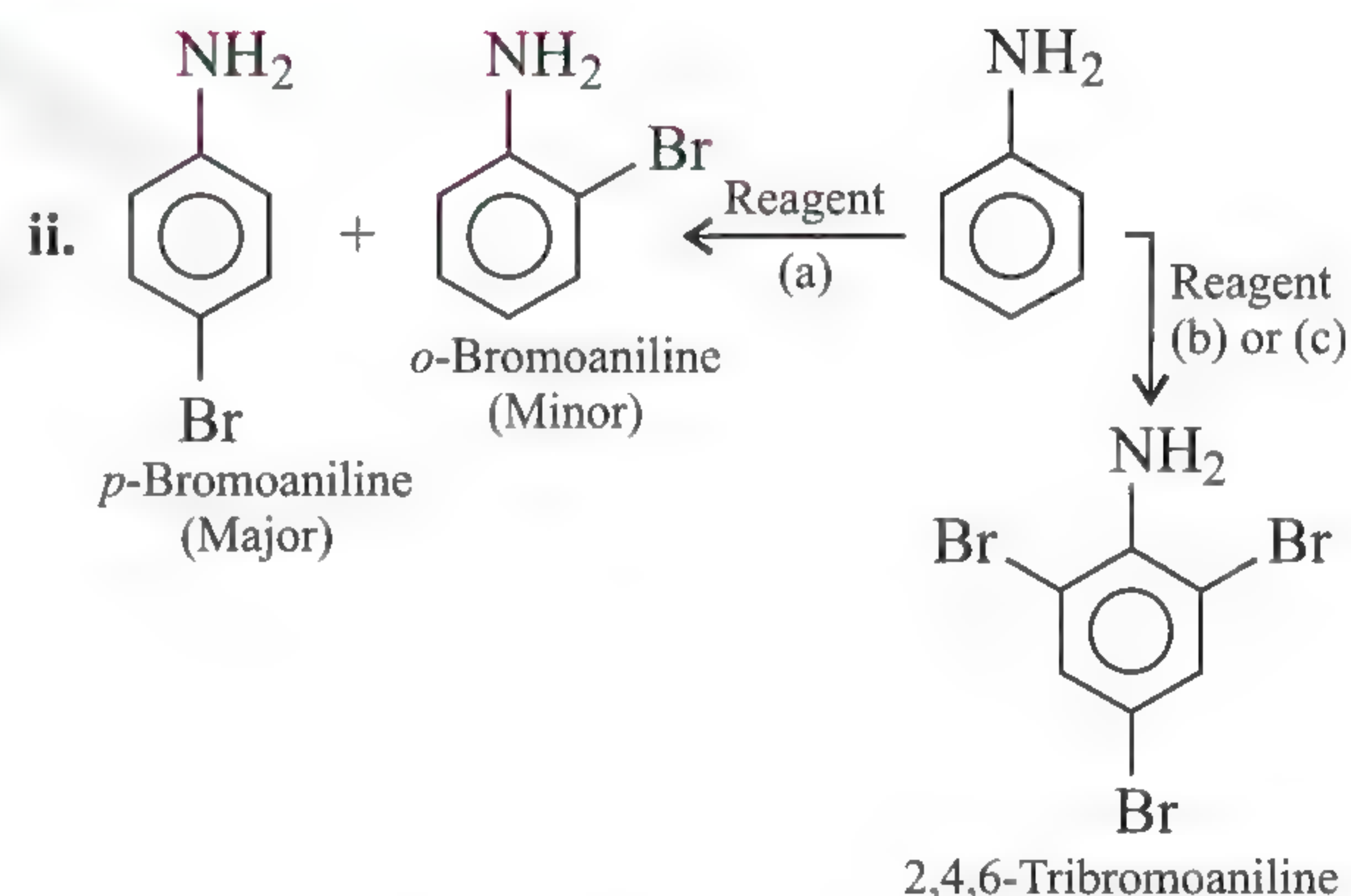
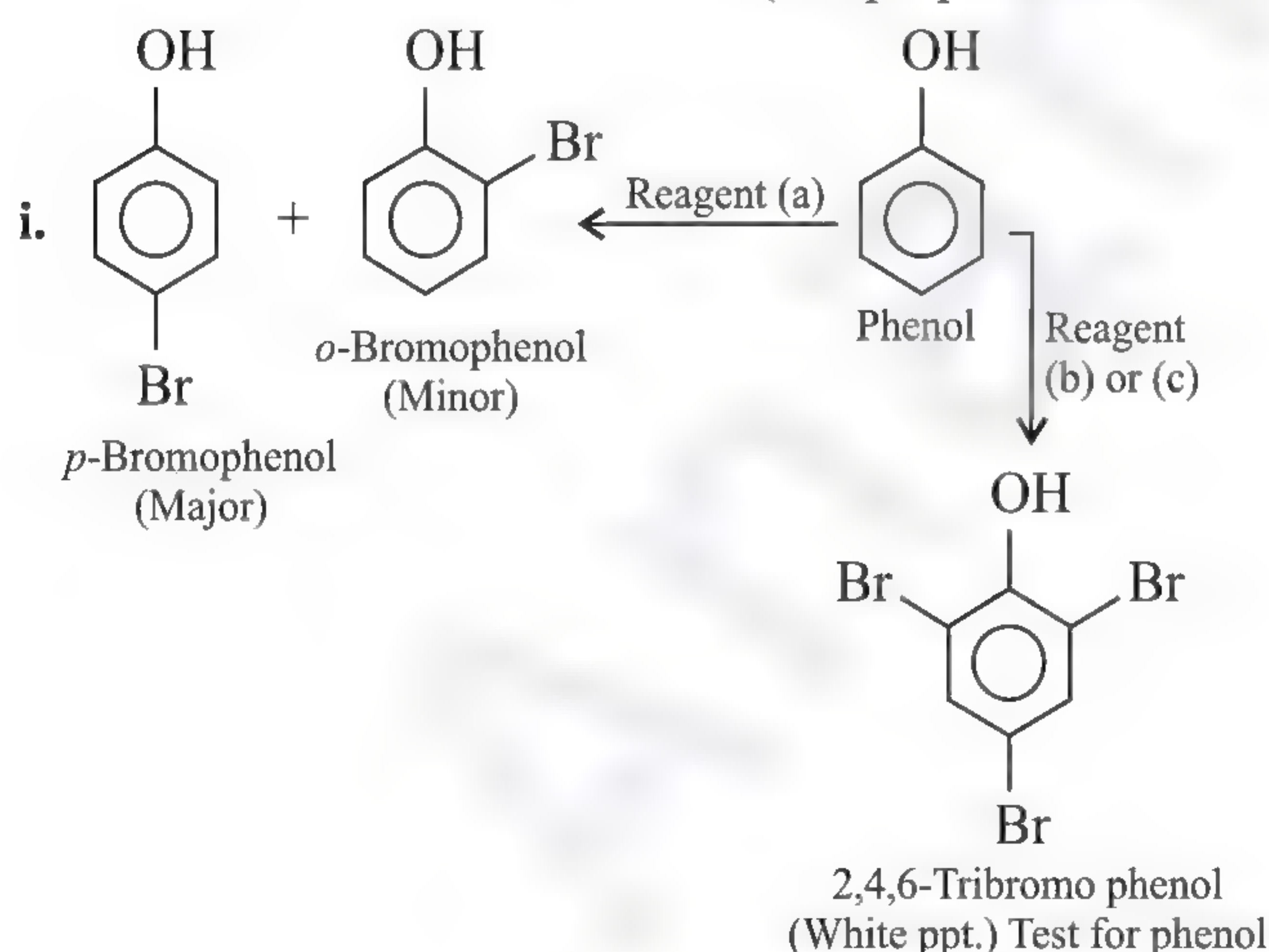
3.14.1 HALOGENATION OF PHENOL, ANILINE AND THEIR DERIVATIVES

Bromination can be carried out with any of the following reagents:

- Br_2 in non-polar solvents (CS_2 or CHCl_3) at low temperature gives *o*- and *p*-products.
- Br_2 in polar solvent (H_2O or glacial acetic acid) gives tribromo product.
- With brominating reagent ($\text{KBrO}_3 + \text{KBr} + \text{H}^+$) also gives tribromo product.



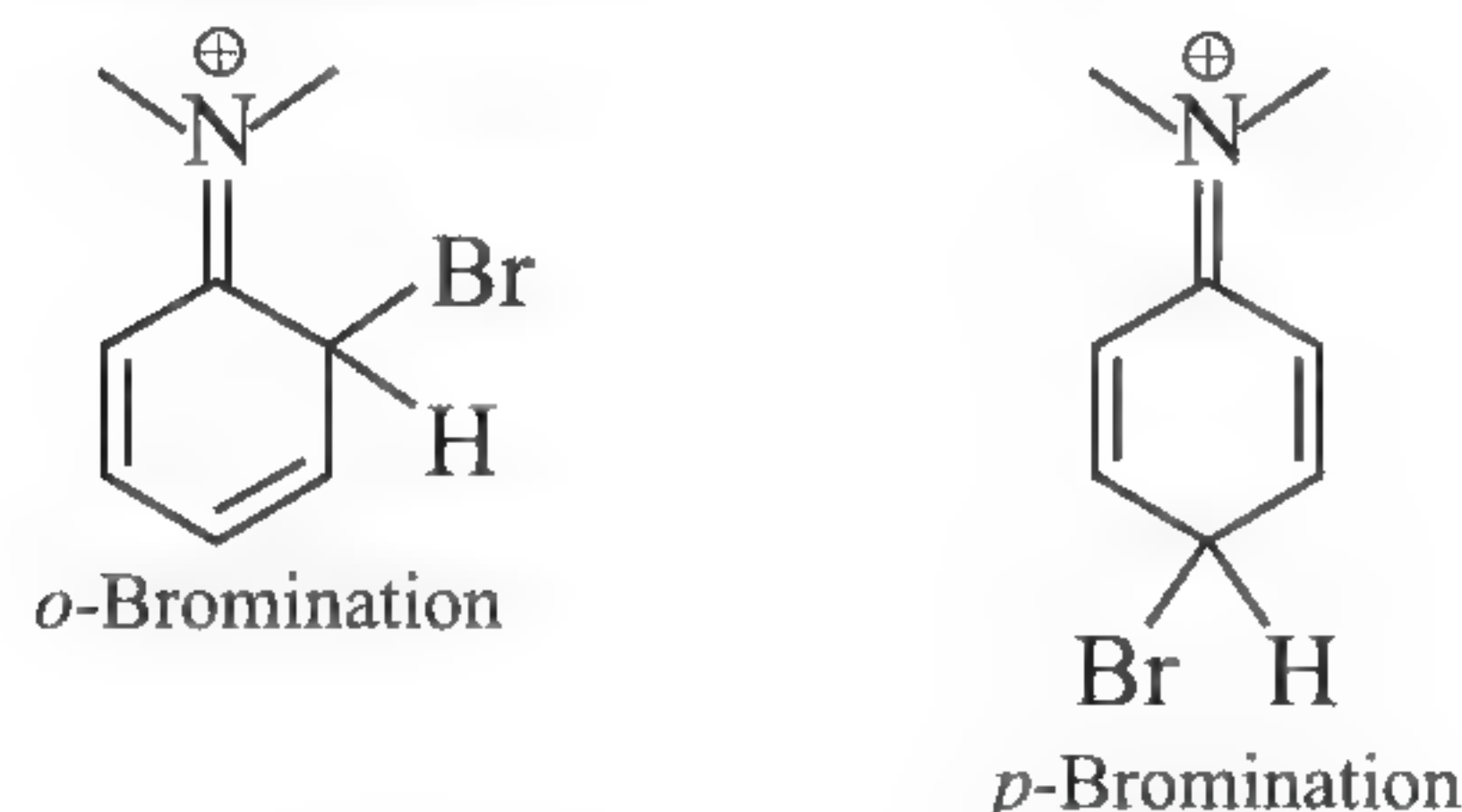
(Conproportionation reaction)



Explanation:

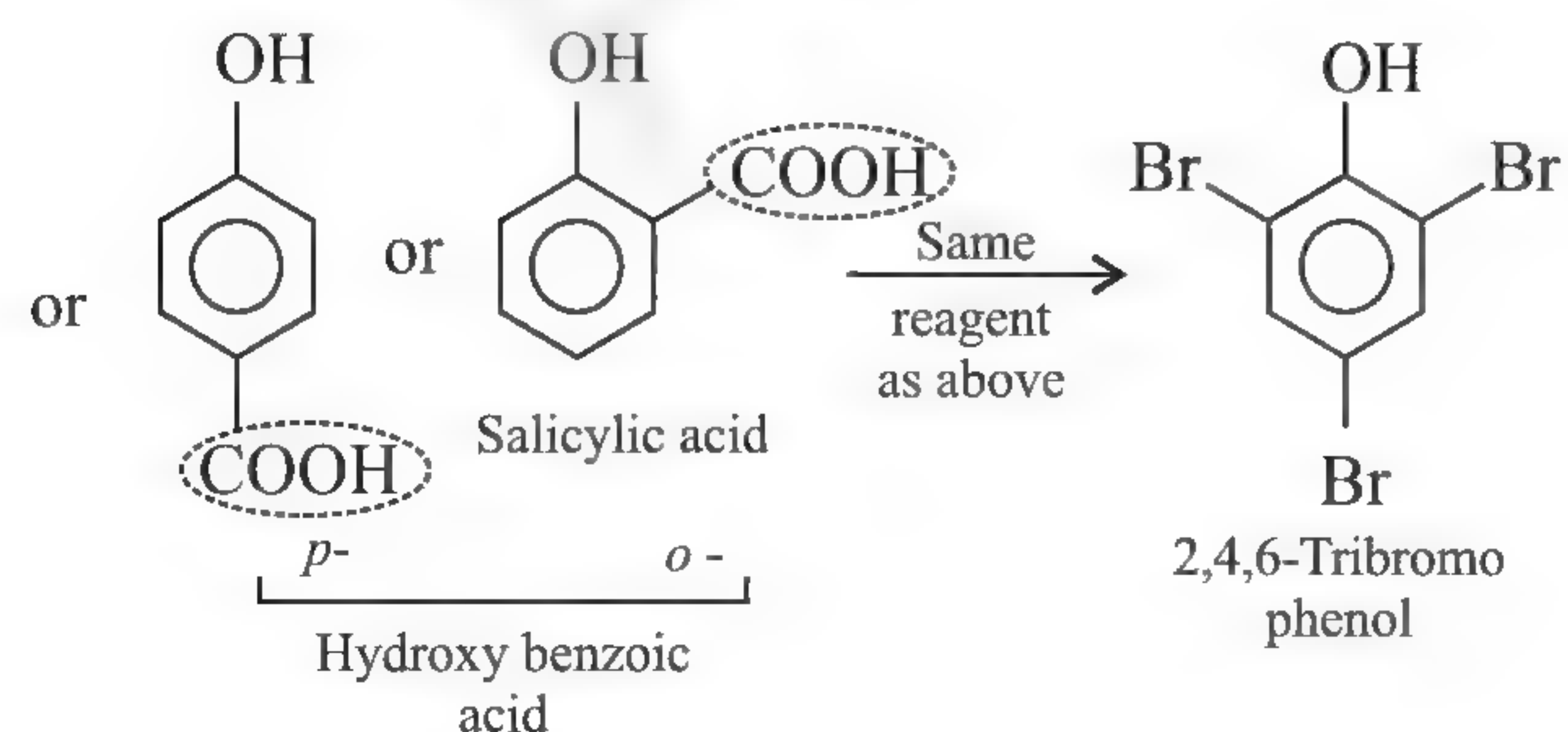
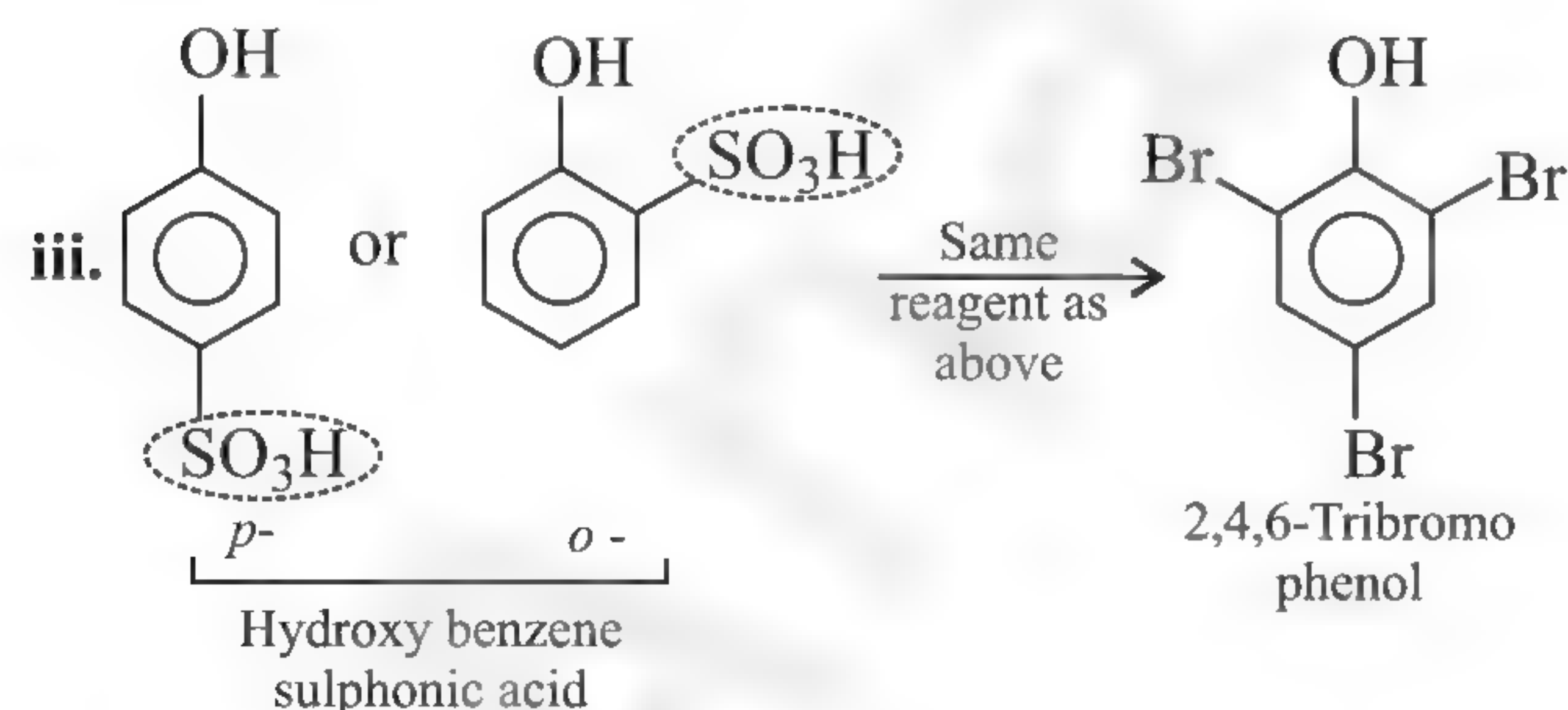
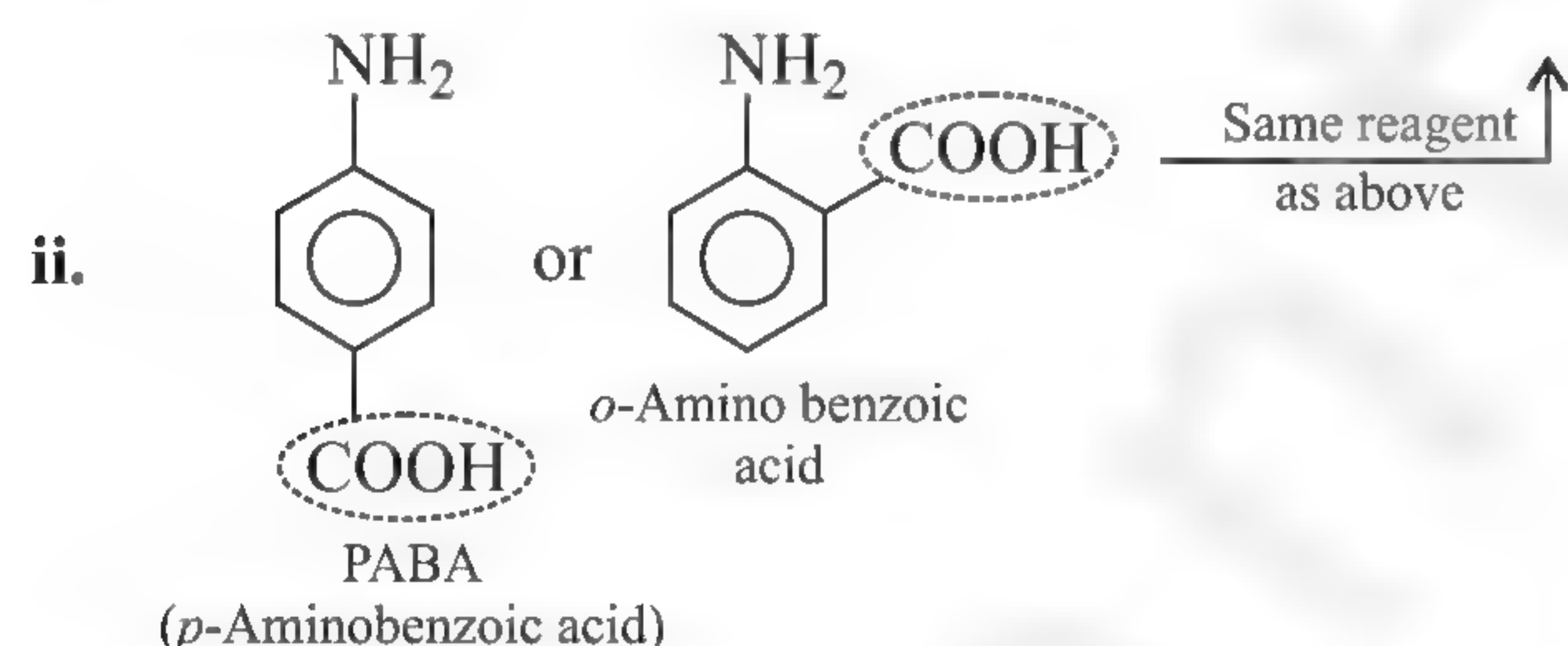
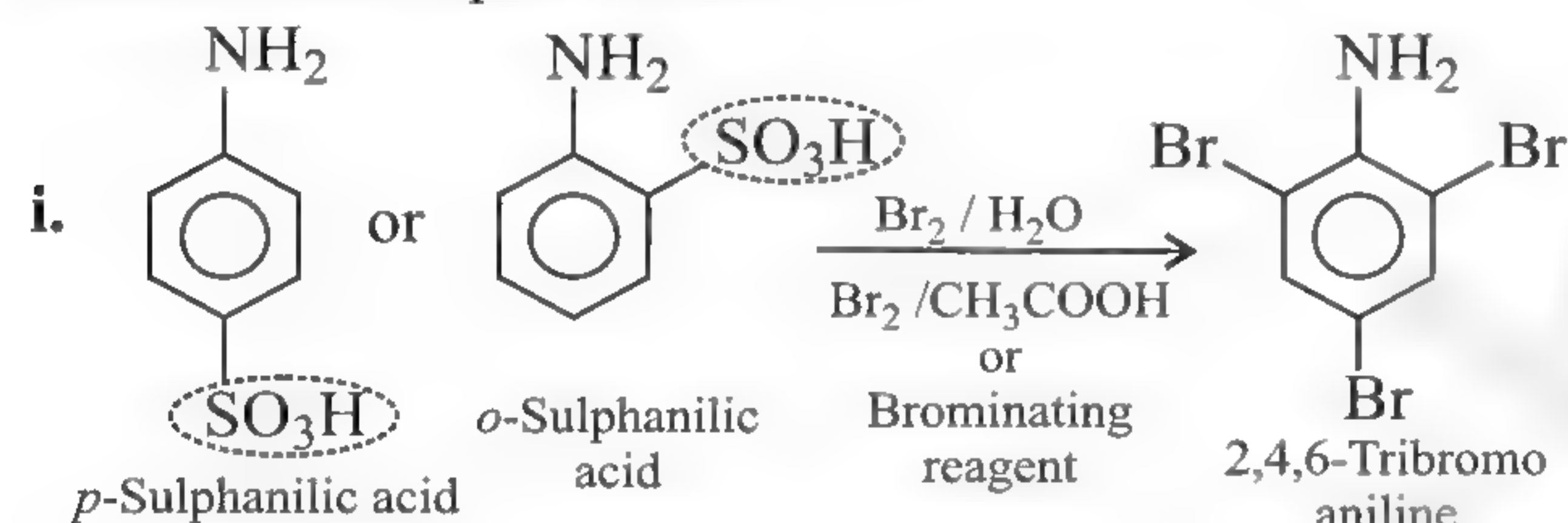
- In aqueous solution, Br_2 is polarised to give Br^+ and Br^- . So, the generation of electrophile Br^+ is very fast and SE reaction proceeds with ease.
- Due to high \bar{e} -donating power of ($-\text{OH}$) and ($-\text{NH}_2$) groups, phenol and aniline are resonance stabilised. Consequently, benzene ring gets highly activated at all the *ortho* and *para* positions, and hence trisubstitution occurs.
- In non-polar solvents such as CS_2 , CHCl_3 , CCl_4 , etc., the polarisation of Br_2 is very slow, so the generation of electrophile Br^+ is very slow and SE reaction is also slow; so only monosubstitution products are formed.
- Also, in non-polar solvents, the ionisation of phenol is suppressed. As a result, oxygen of the (OH) group donates \bar{e} to the benzene ring to a small extent. Consequently, the ring is activated only slightly and hence only monosubstitution products are formed.

- v. This high reactivity is due to the fact that in addition to other resonating structures that stabilise intermediate carbonium ion in aromatic electrophilic substitution, following structures are formed due to the interaction of nitrogen unshared pair of electrons, with the positively charged ring also contribute to the stability of the intermediates in *o*-, *p*-bromination.

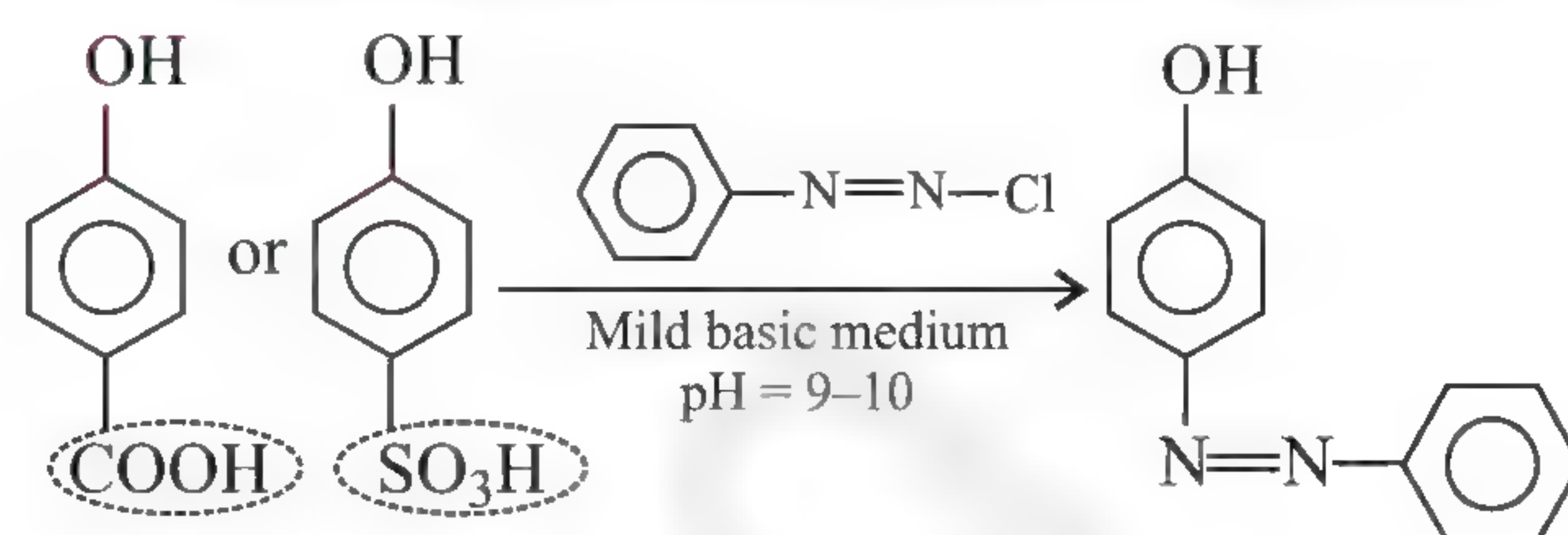


3.15 IPSO SUBSTITUTION

- a. When (—COOH) or ($\text{—SO}_3\text{H}$) OR ($\text{—N}\equiv\text{N—}$) group is present in the *ortho*- or *para*-position in phenol or aniline, these groups are replaced or substituted by the incoming electrophile E^+ during SE reaction of phenol or aniline. The displacement of one ring substituent by another is called an **ipso substitution**. The C atom where such a substitution occurs is called ipso C atom.

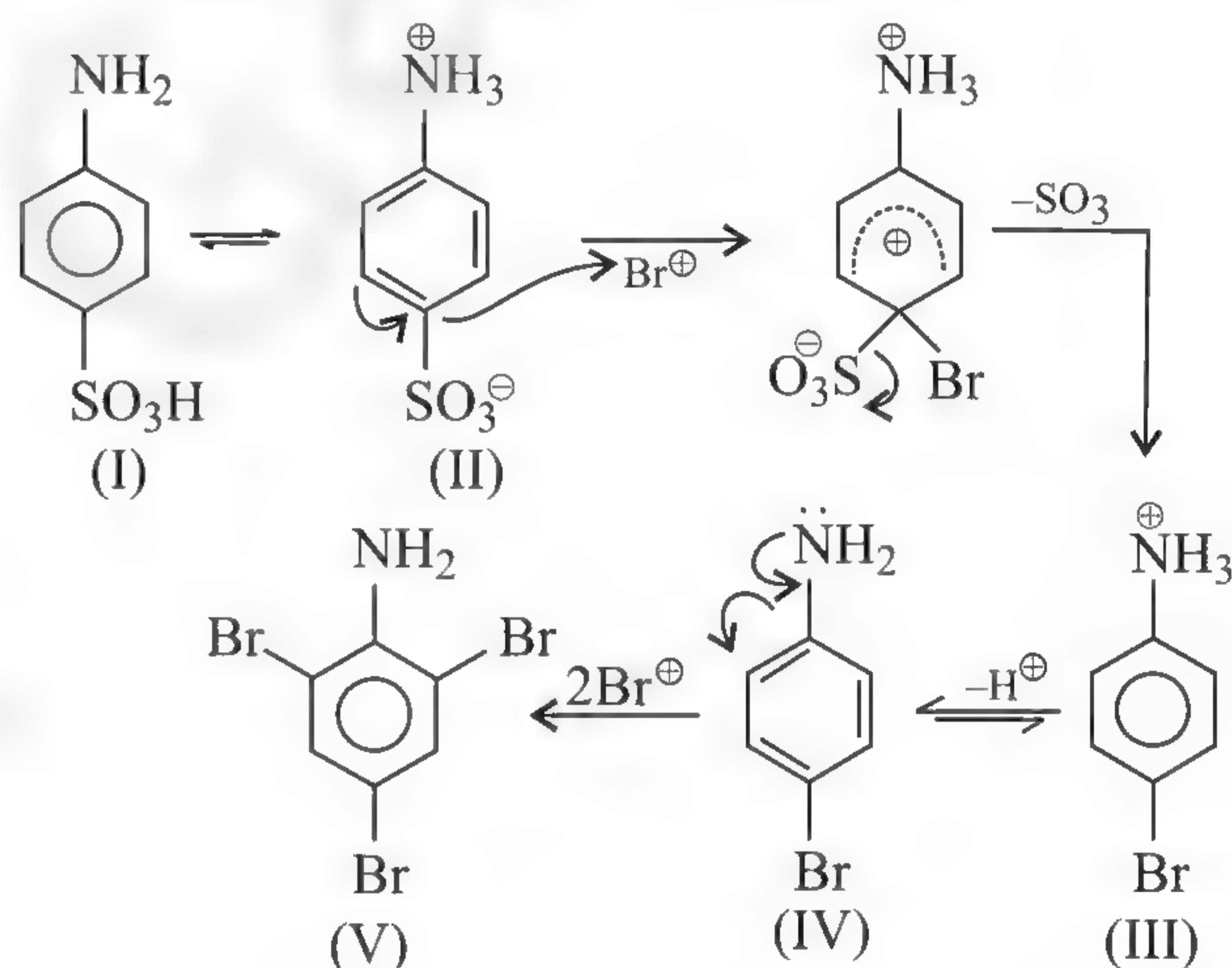


- iv. In cases where a (—COOH) or ($\text{—SO}_3\text{H}$) group is present in *p*-position to (—OH) or (—NH_2) group, it is replaced by an azo group during coupling.

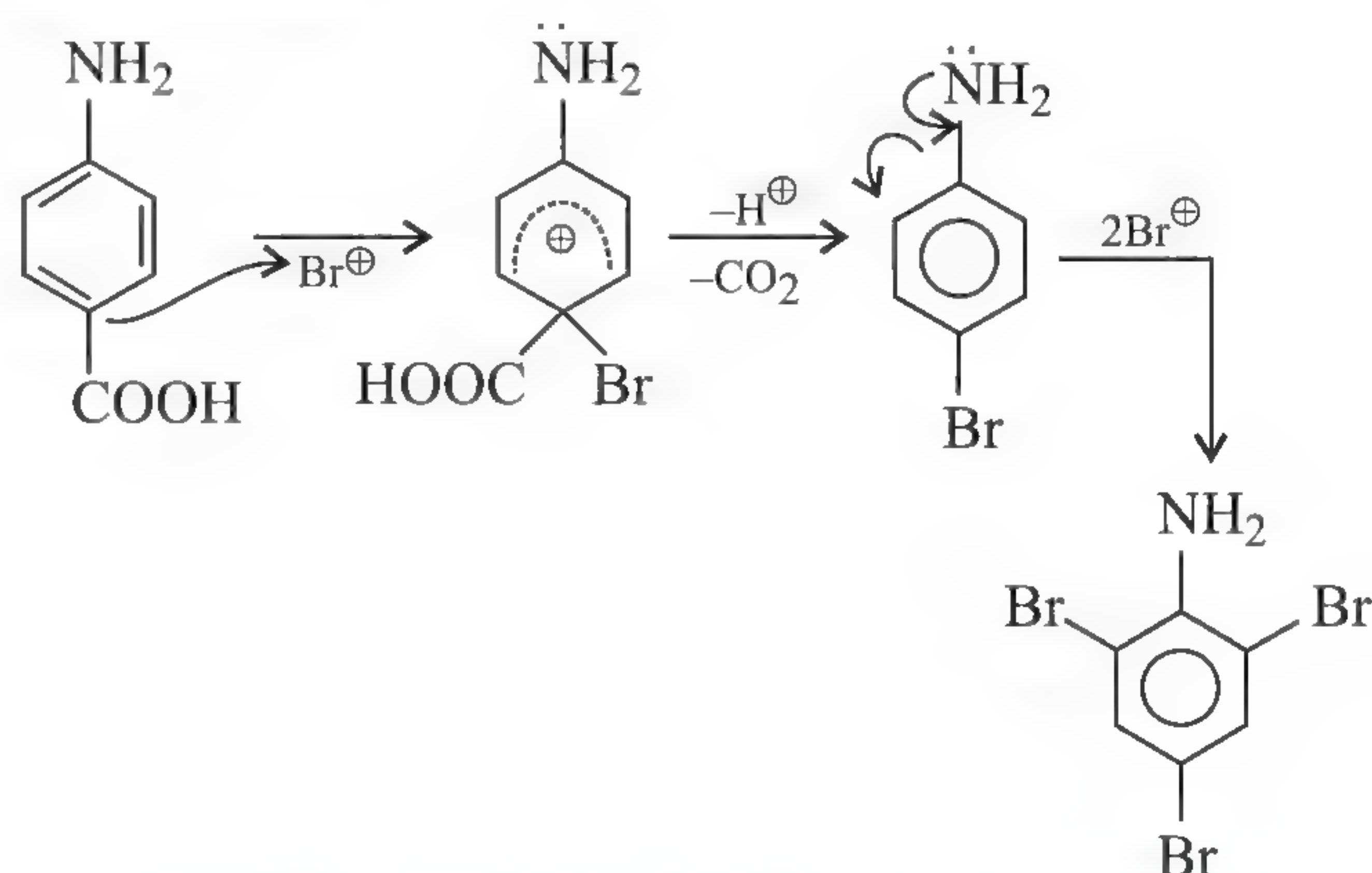


b. Mechanism:

In *p*-sulphanilic acid (I), zwitterion (II) exists. Electrophile (Br^+) attacks the ring C atom, displacing SO_3 (a good leaving group) to form (III), which is a strong acid and is converted to amino group in (IV). The (—NH_2) group in (IV) is EDG and activates the ring to further substitution by (Br^+) in the two *ortho*- positions to form the product (V).



A similar reaction occurs with PABA in which CO_2 is lost, also a good leaving group (PABA does not exist as zwitterion or dipolar ion).



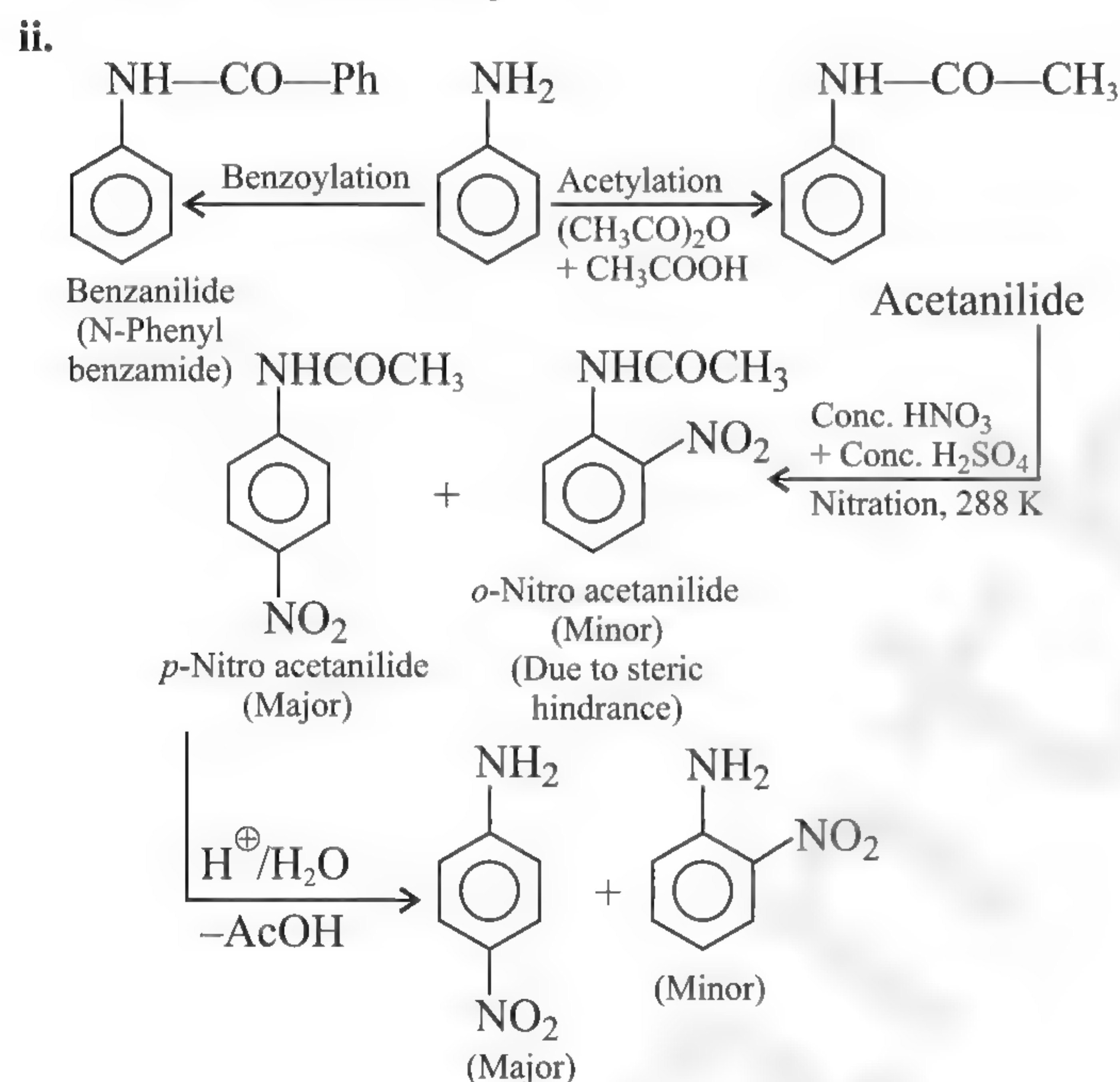
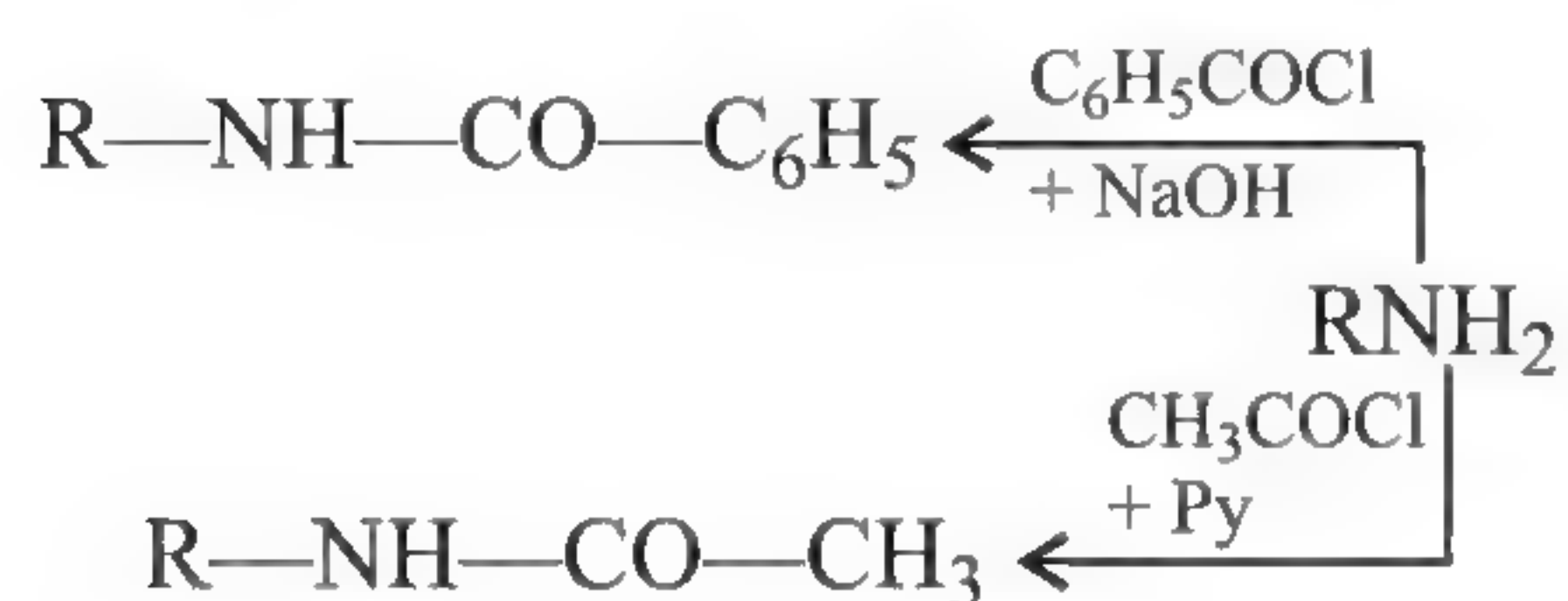
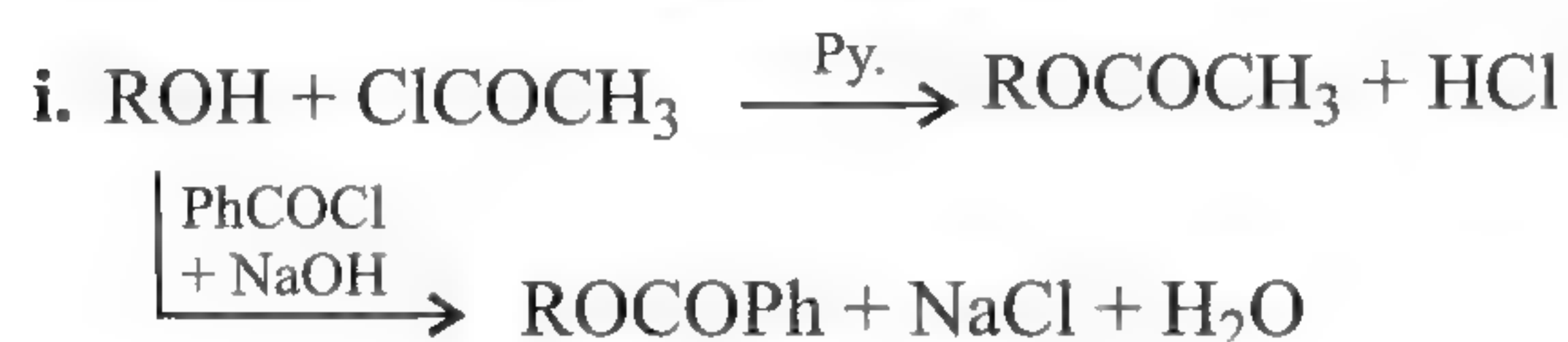
3.16 ACETYLATION, BENZOYLATION AND TOSYLATION

To avoid the oxidation of aniline and phenol by nitration, the amino and (—OH) groups are protected by acetylation benzylation or tosylation. The acetyl or benzoyl group is finally removed by hydrolysis to give *o*- and *p*-isomers.

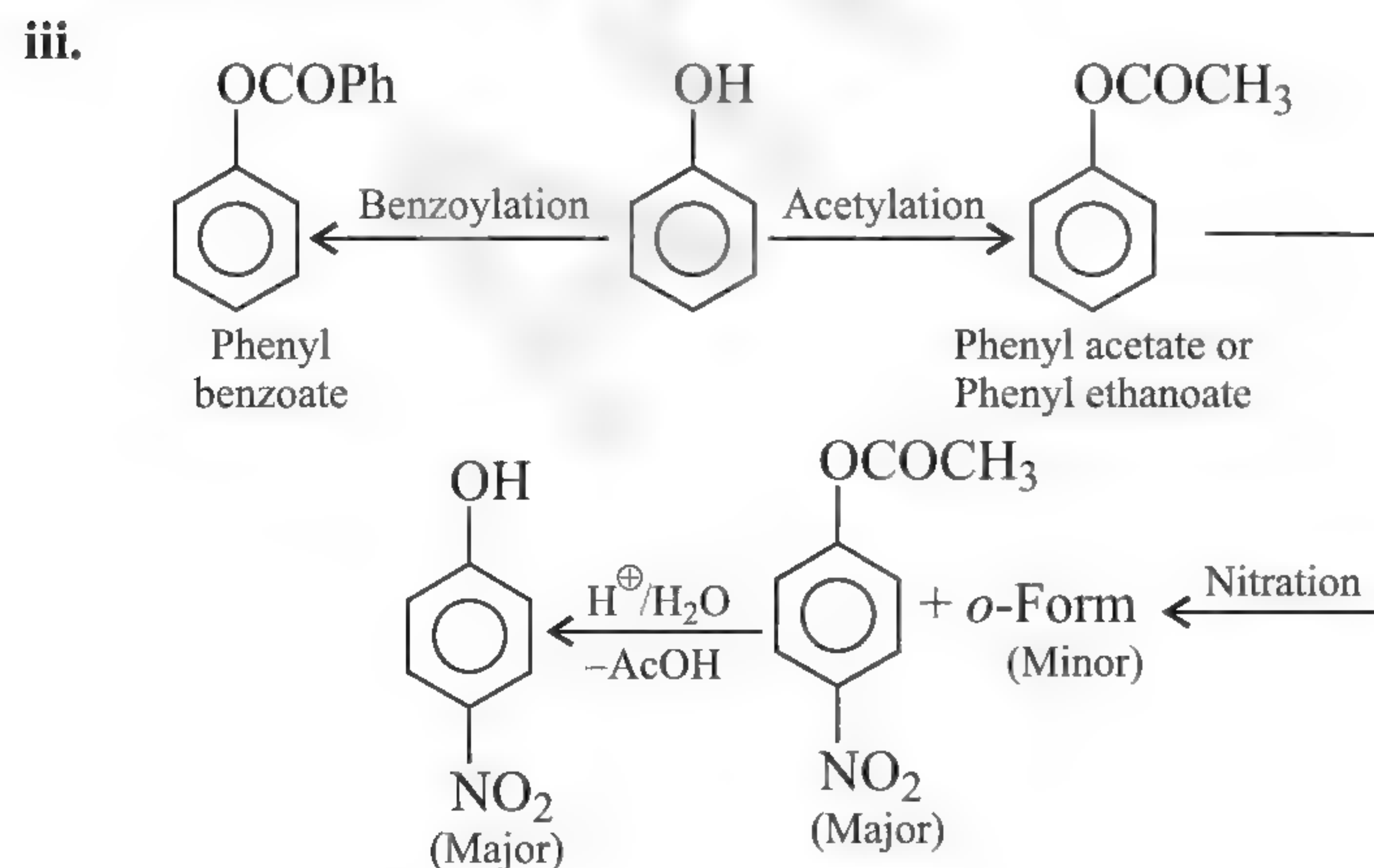
a. Acetylation can be done by any of the following three acetylating reagents.

- $(\text{CH}_3\text{CO})_2\text{O} + \text{Glacial acetic acid}$
- $(\text{CH}_3\text{CO})_2\text{O} + \text{Conc. H}_2\text{SO}_4$
- $\text{CH}_3\text{COCl} + \text{Pyridine}$

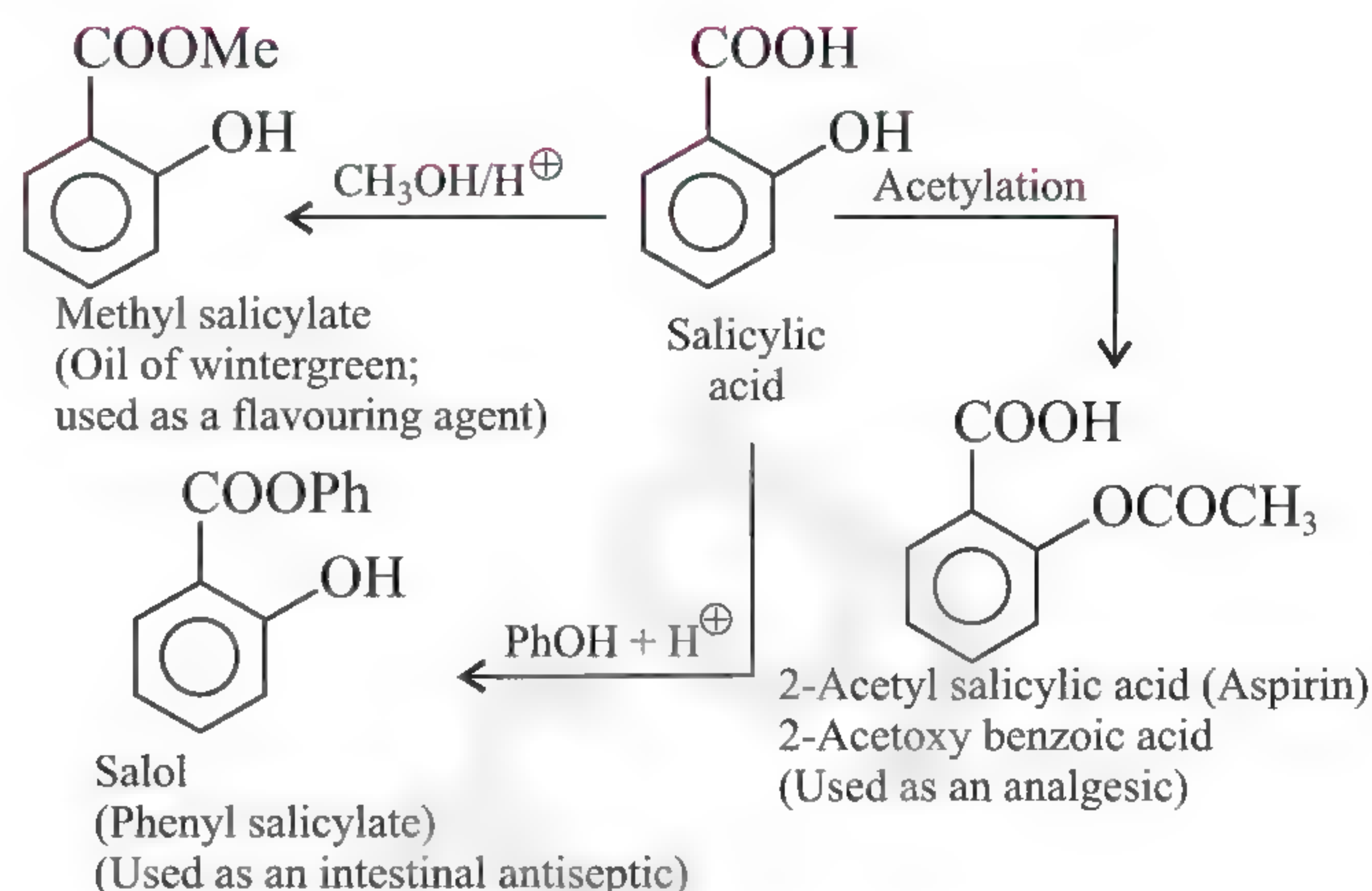
b. The benzoylation of alcohol, phenol, aromatic, or aliphatic amine with benzoyl chloride ($\text{C}_6\text{H}_5\text{COCl}$) and NaOH is called Schotten–Baumann reaction.



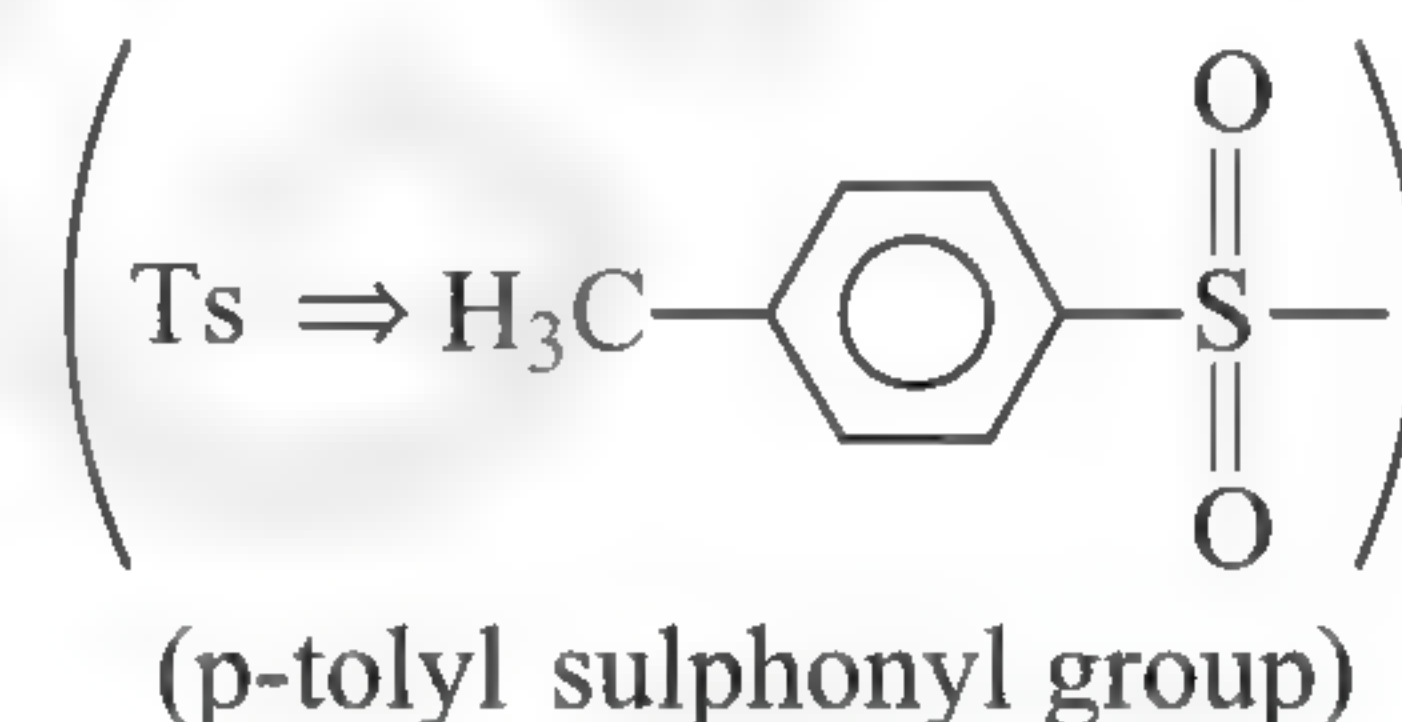
Acetanilide was the first compound used as an antipyretic sold under the name **Antifebrin**, but later on it was banned due to its attack on RBC's.



iv.

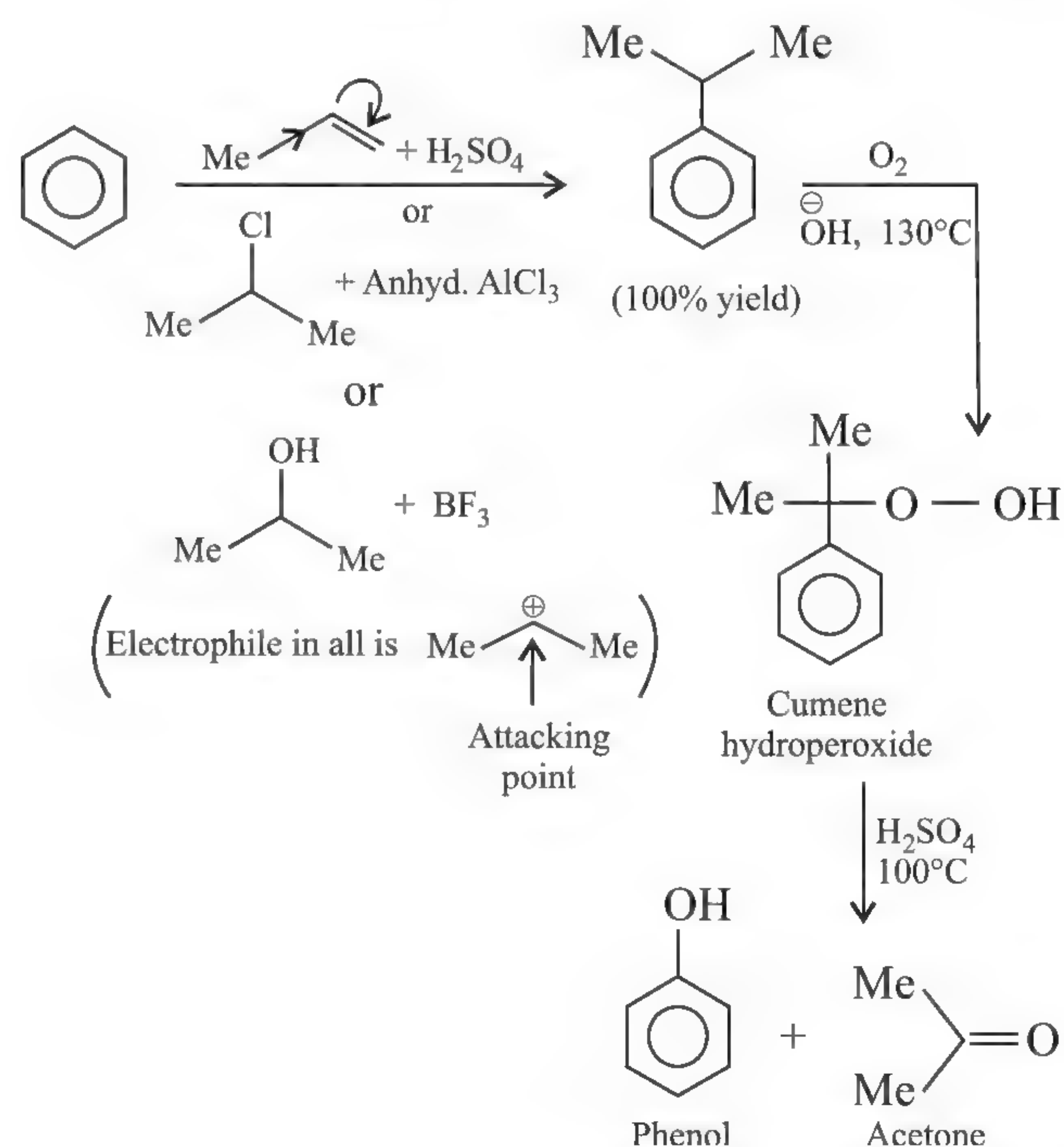


c. Tosylation is done by tosyl chloride with base.

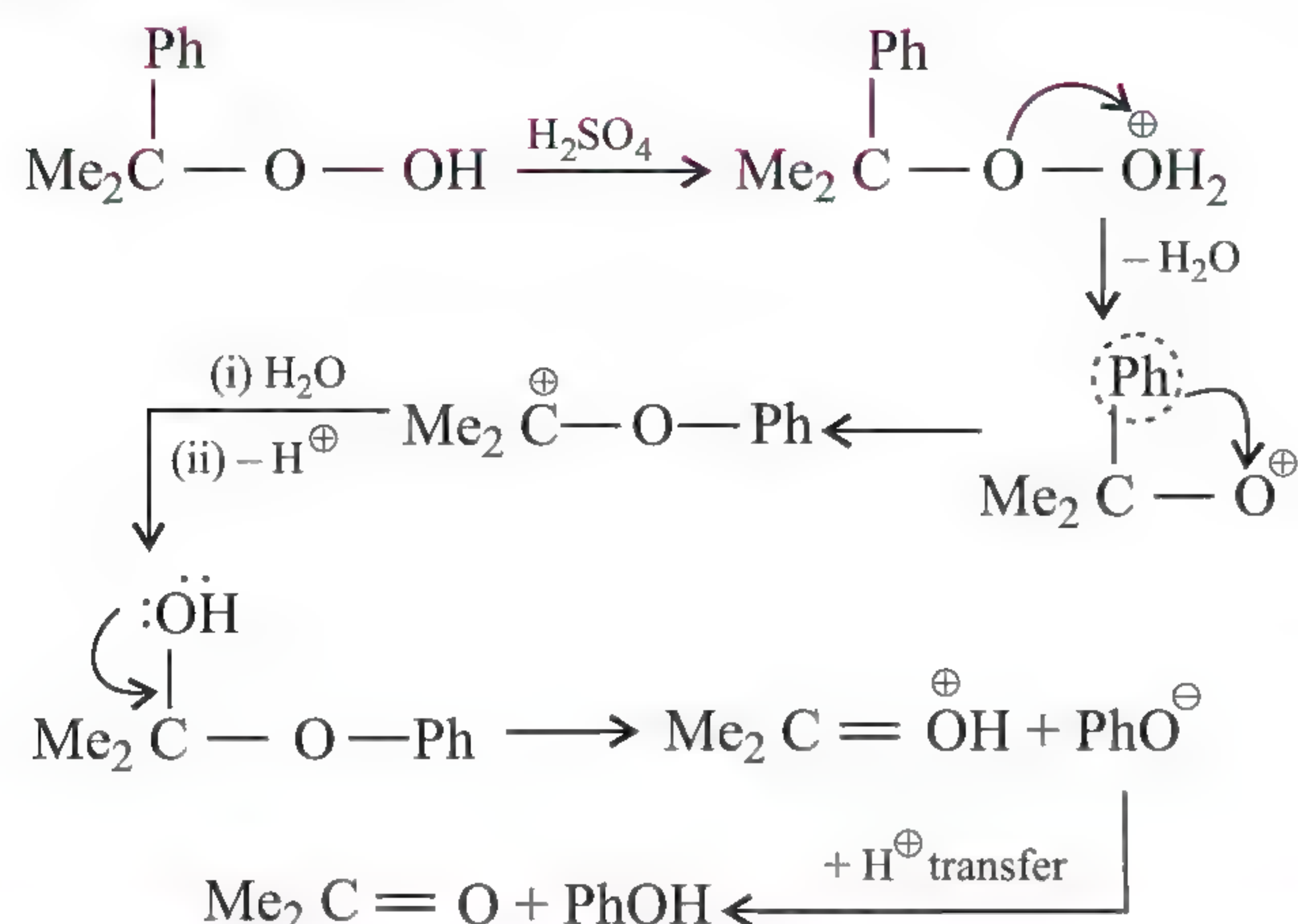


3.17 COMMERCIAL METHOD FOR THE PREPARATION OF PHENOL FROM CUMENE

a. This process is carried out by the aerial oxidation of cumene to hydroperoxide, which is then decomposed by acid into phenol and acetone (byproduct).

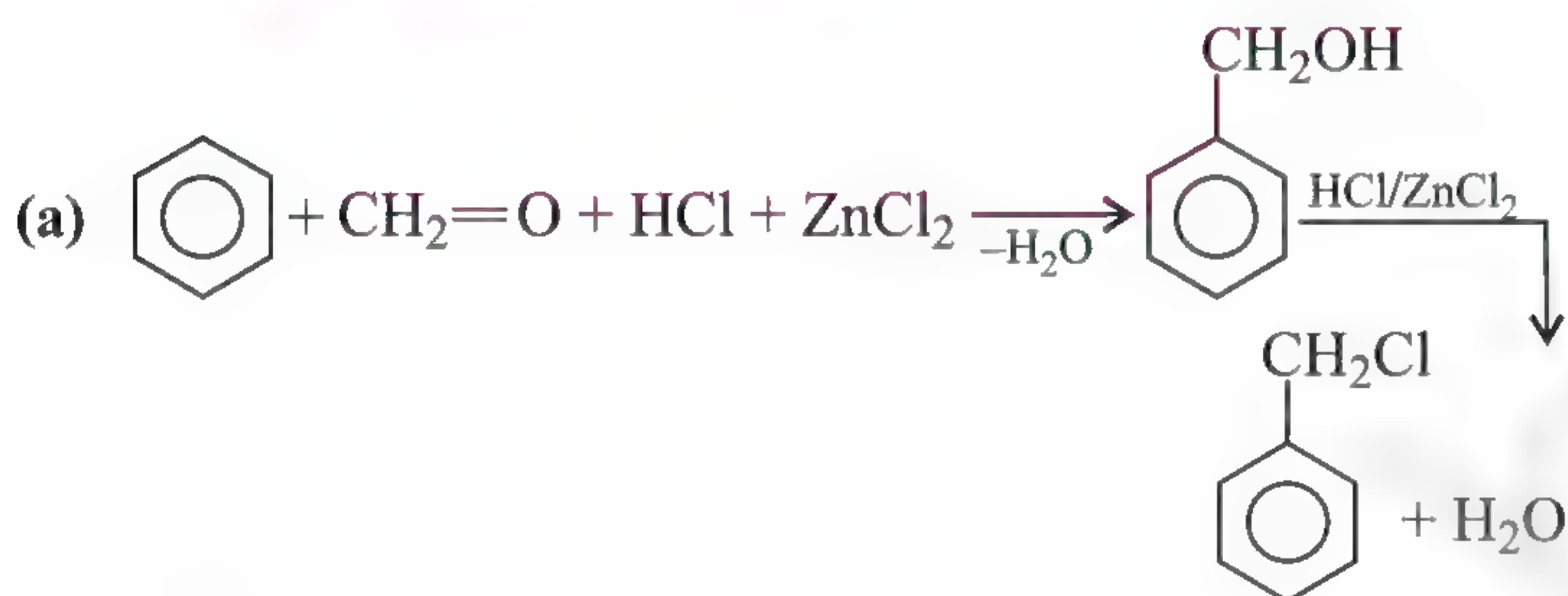


b. Mechanism of conversion of hydroperoxide into phenol and acetone: It takes place by 1,2-shift (e.g., Baeyer–Villiger oxidation).

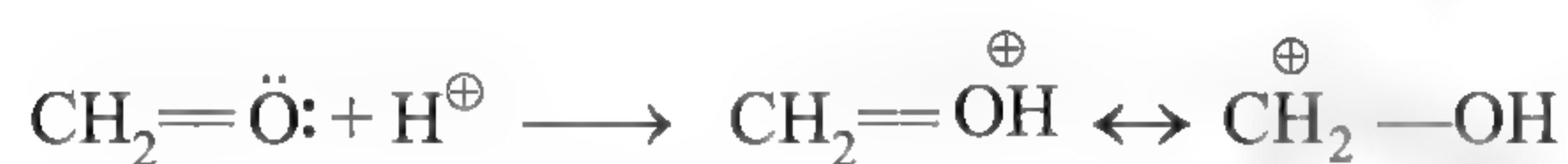


Note: Ph group is a better migrator than Me group even in the presence of two Me— groups.

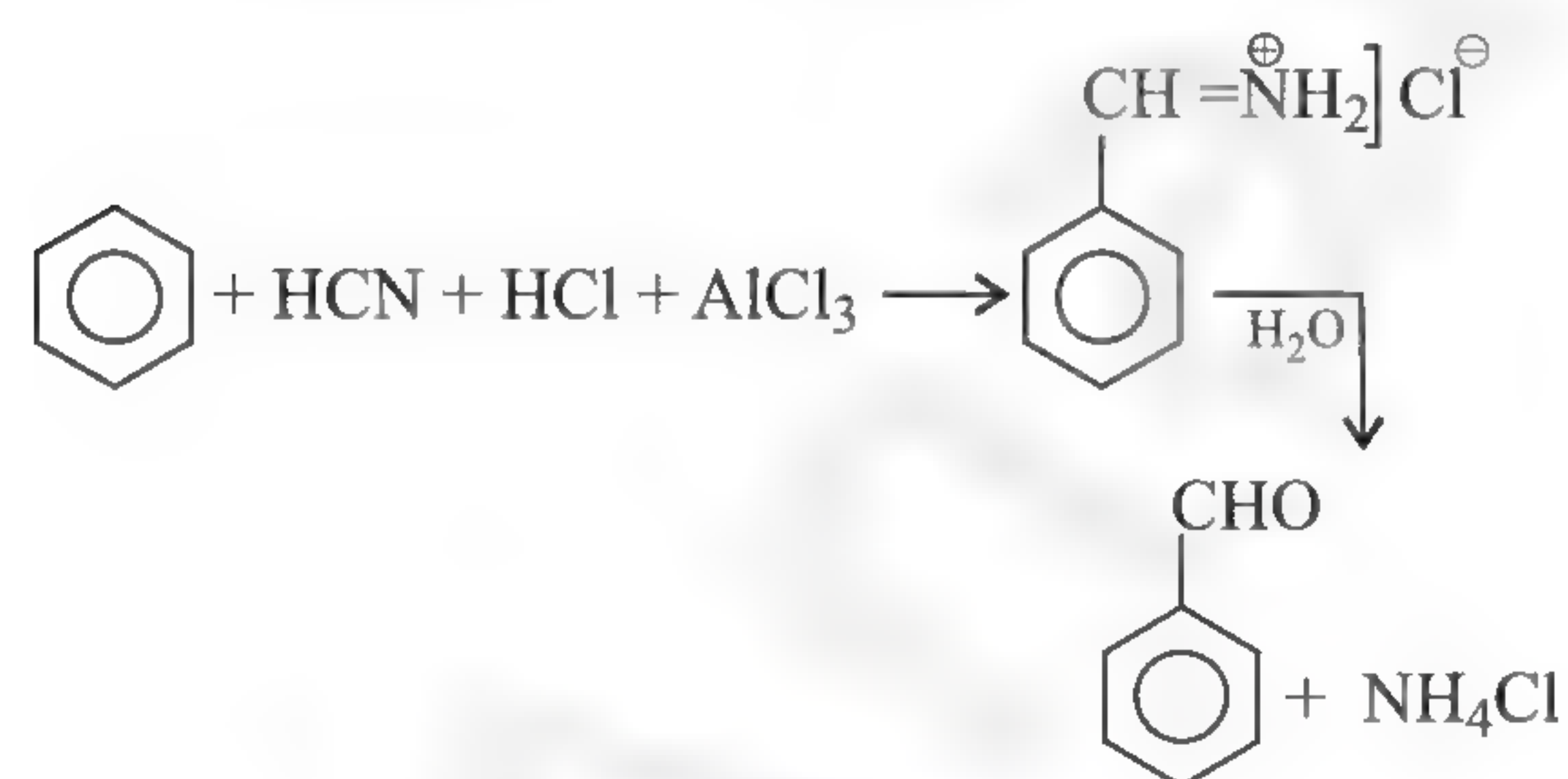
3.18 CHLOROMETHYLATION (SE REACTION)



(b) Mechanism:

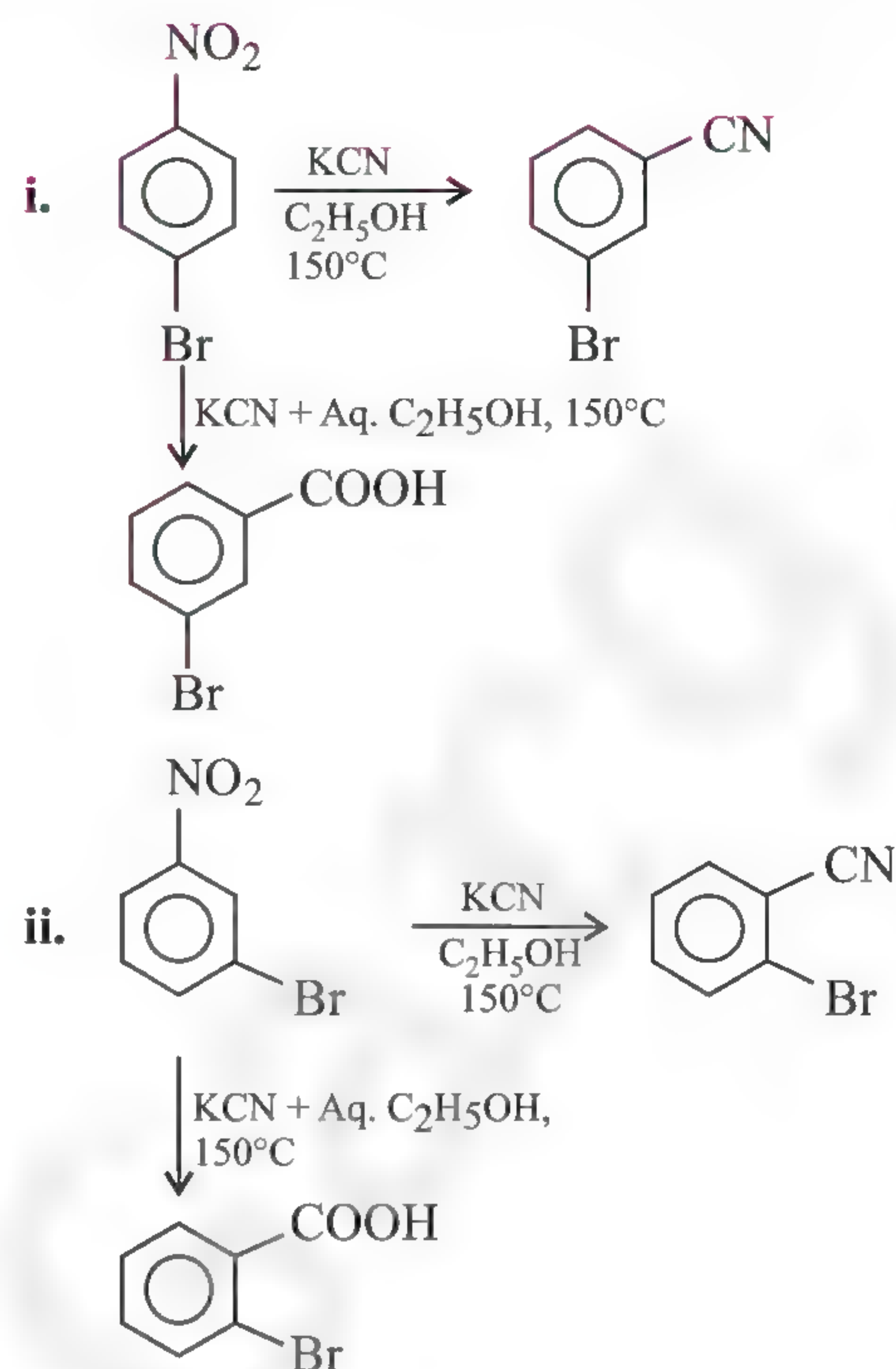


The electrophile is $(\overset{+}{\text{CH}}_2 - \text{OH})$

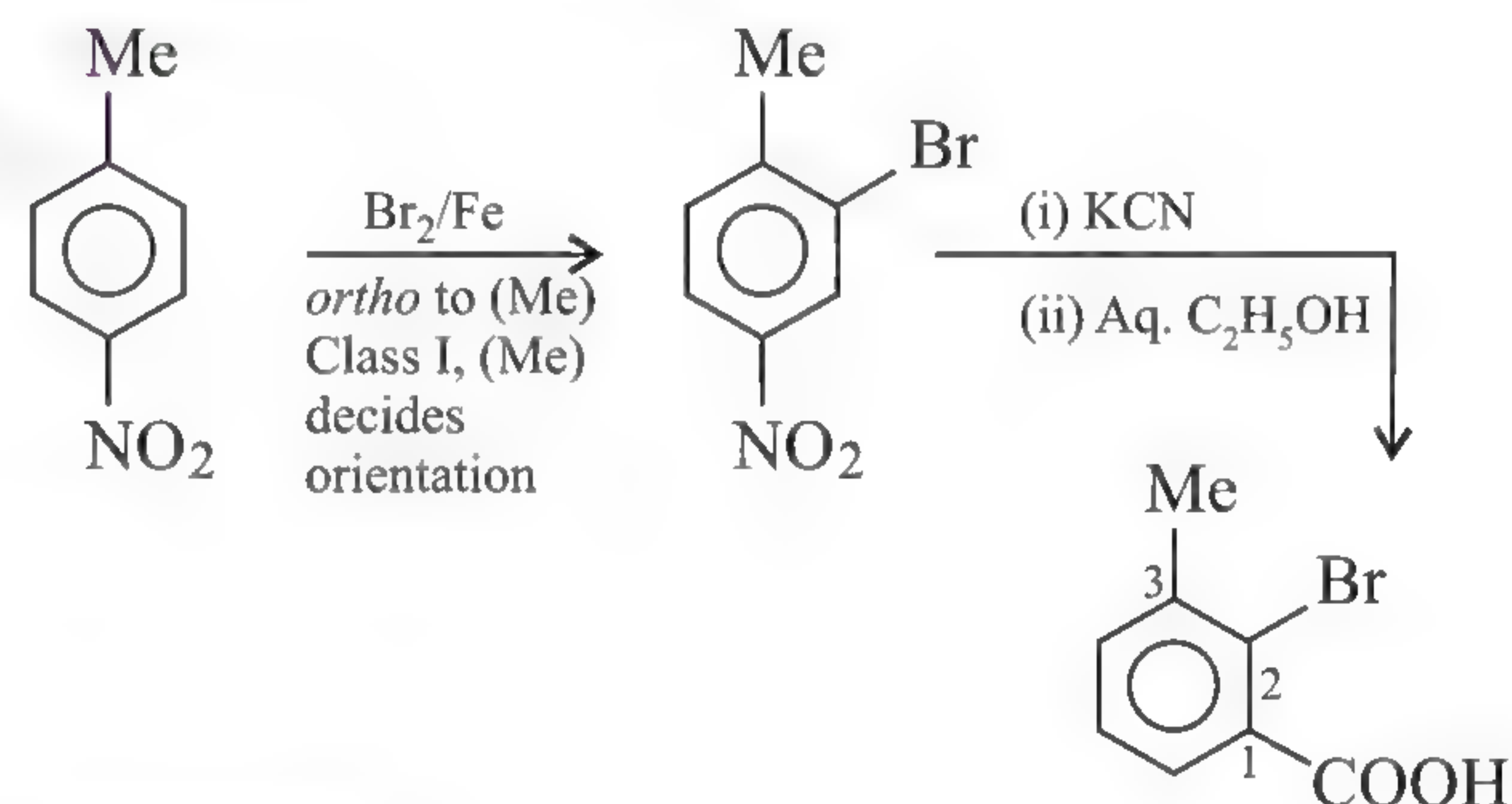


3.19 VON RICHTER REACTION

- (a) When halonitrobenzene is heated with KCN at 150°C, the nitro group is expelled and a cyano group enters the ring *ortho* to the position occupied by the leaving group ($-\text{NO}_2$). This is called Von Richter reaction. It is an example of ArSN with rearrangement.



- (b) **Application of the reaction:** It is used in the preparation of 2-bromo-3-methyl benzoic acid which cannot be prepared by other methods.



(c) Mechanism:

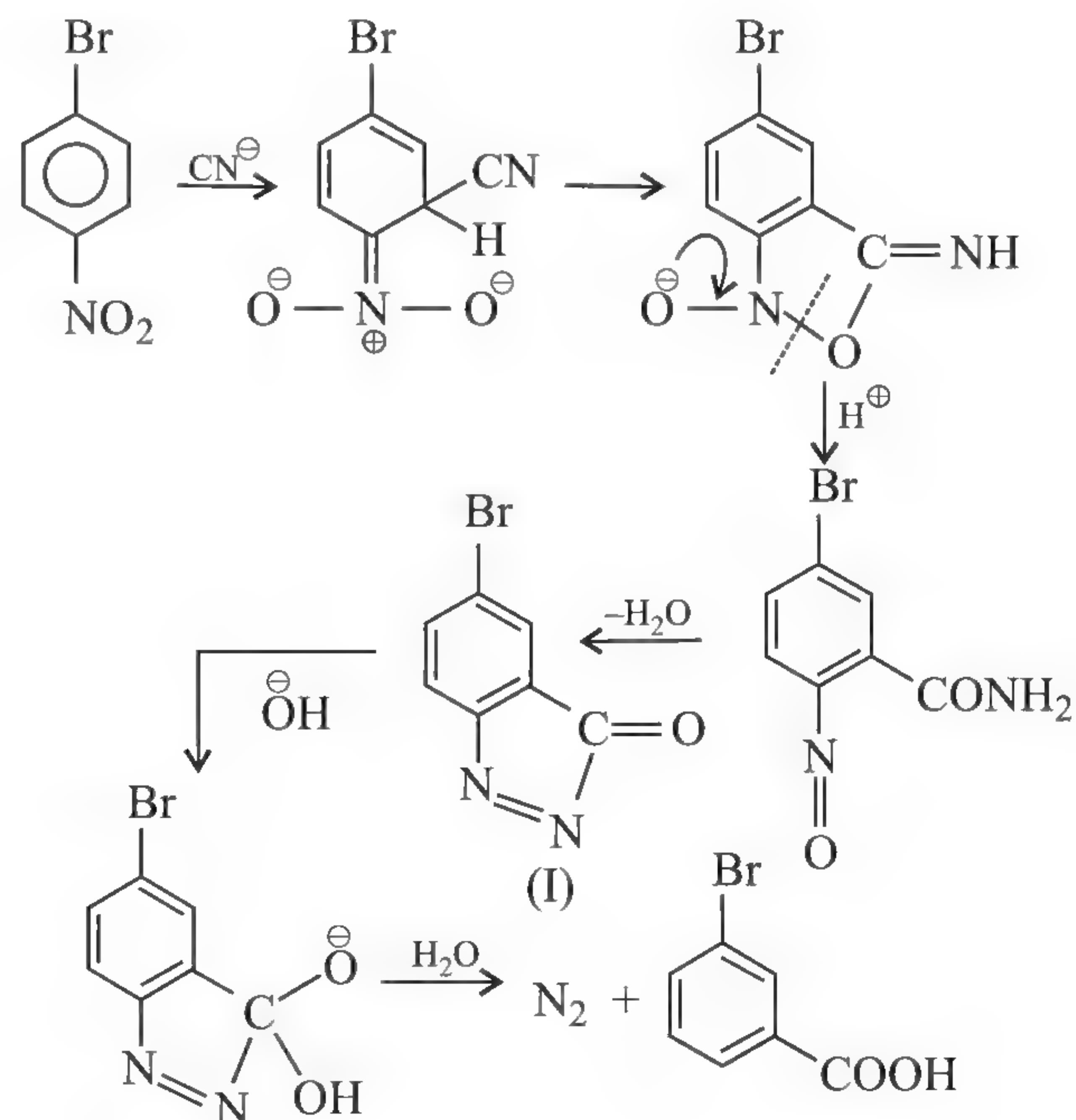
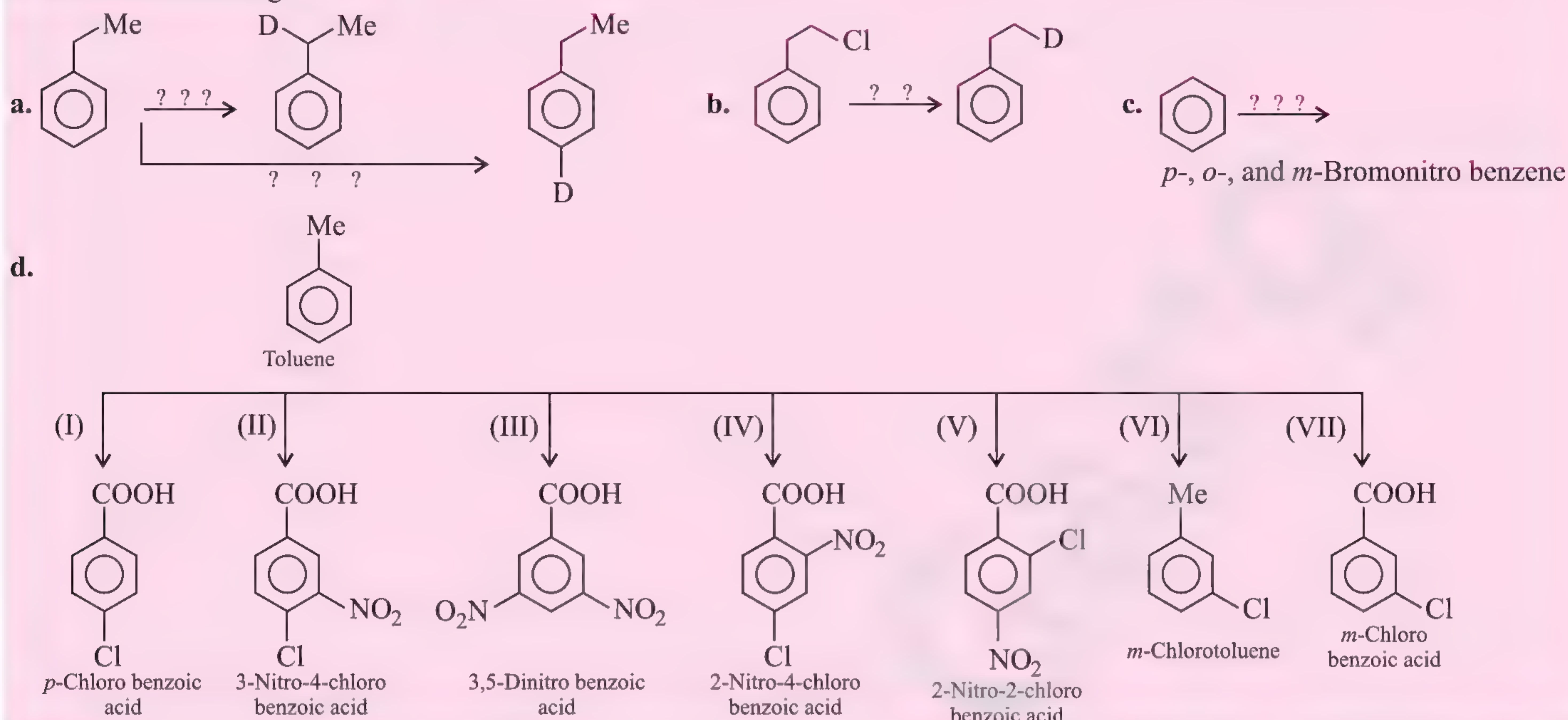
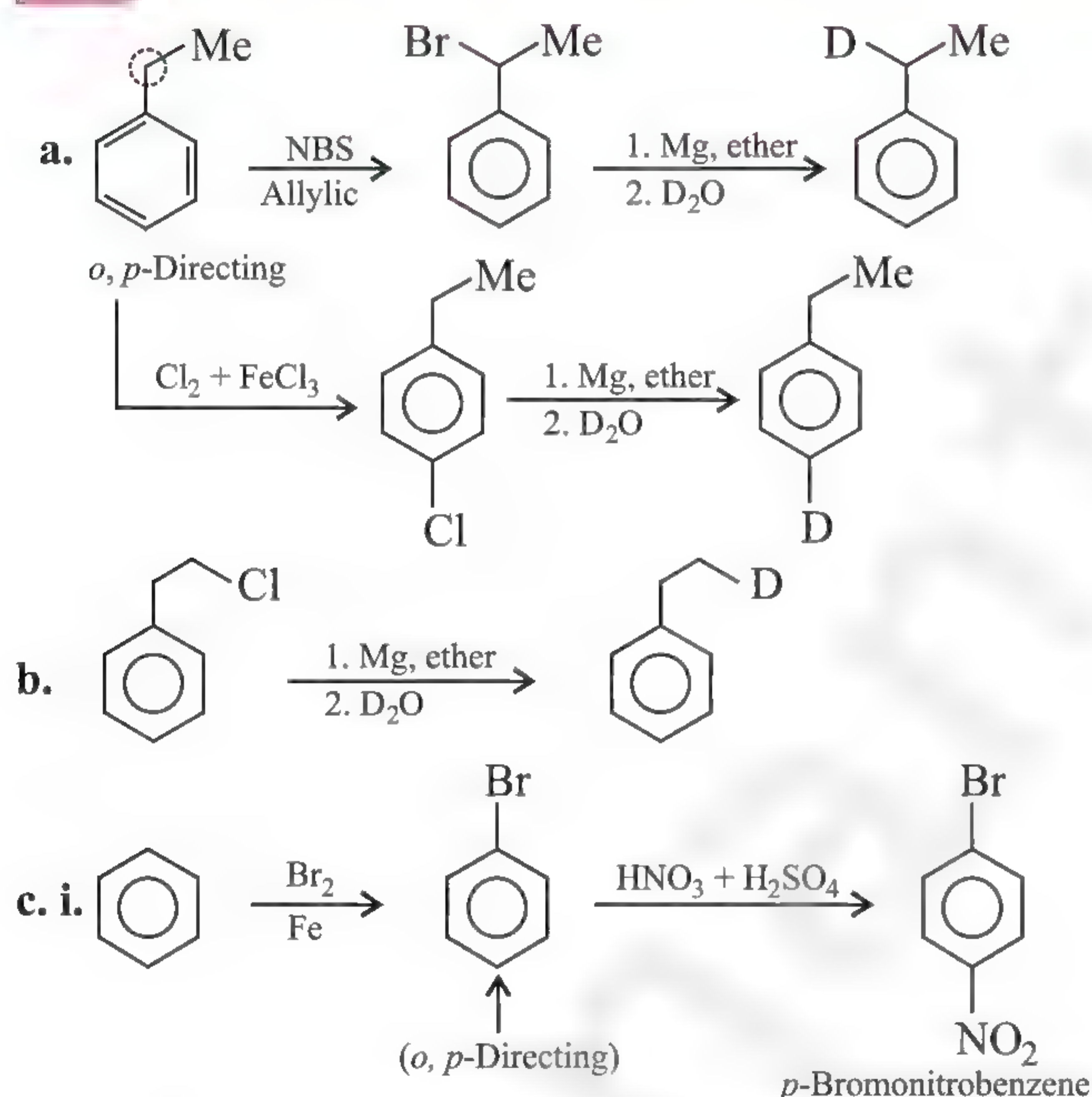
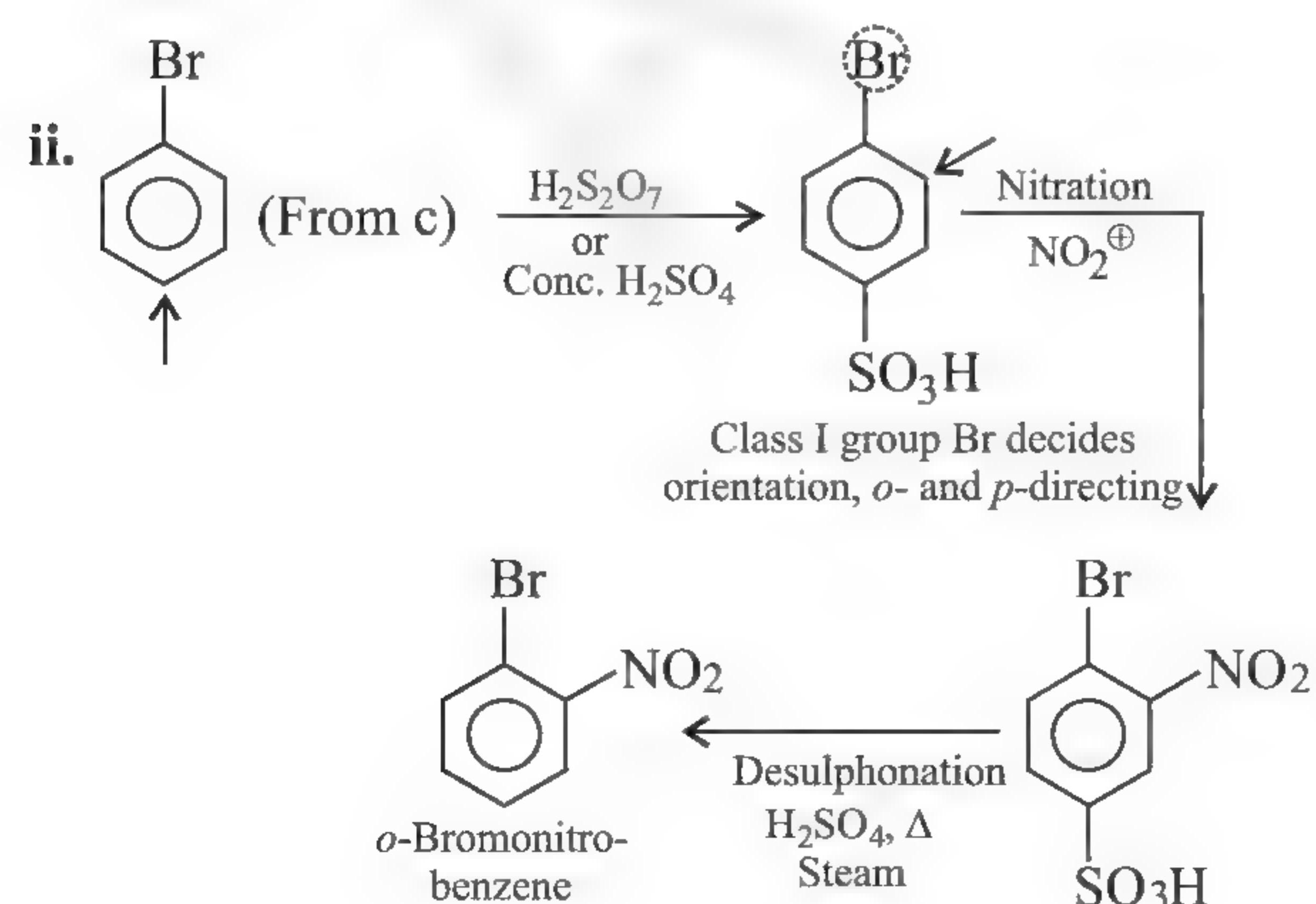
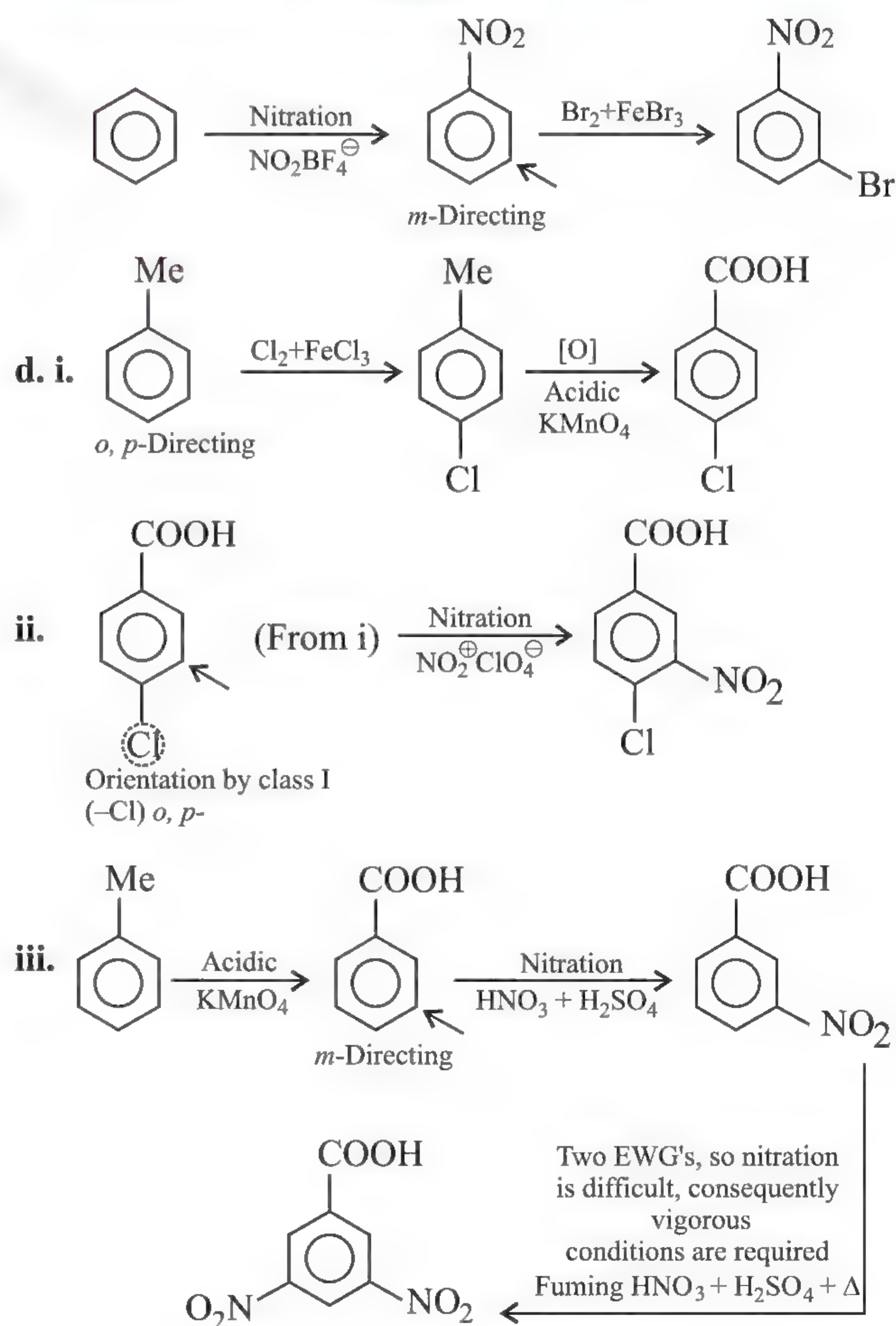


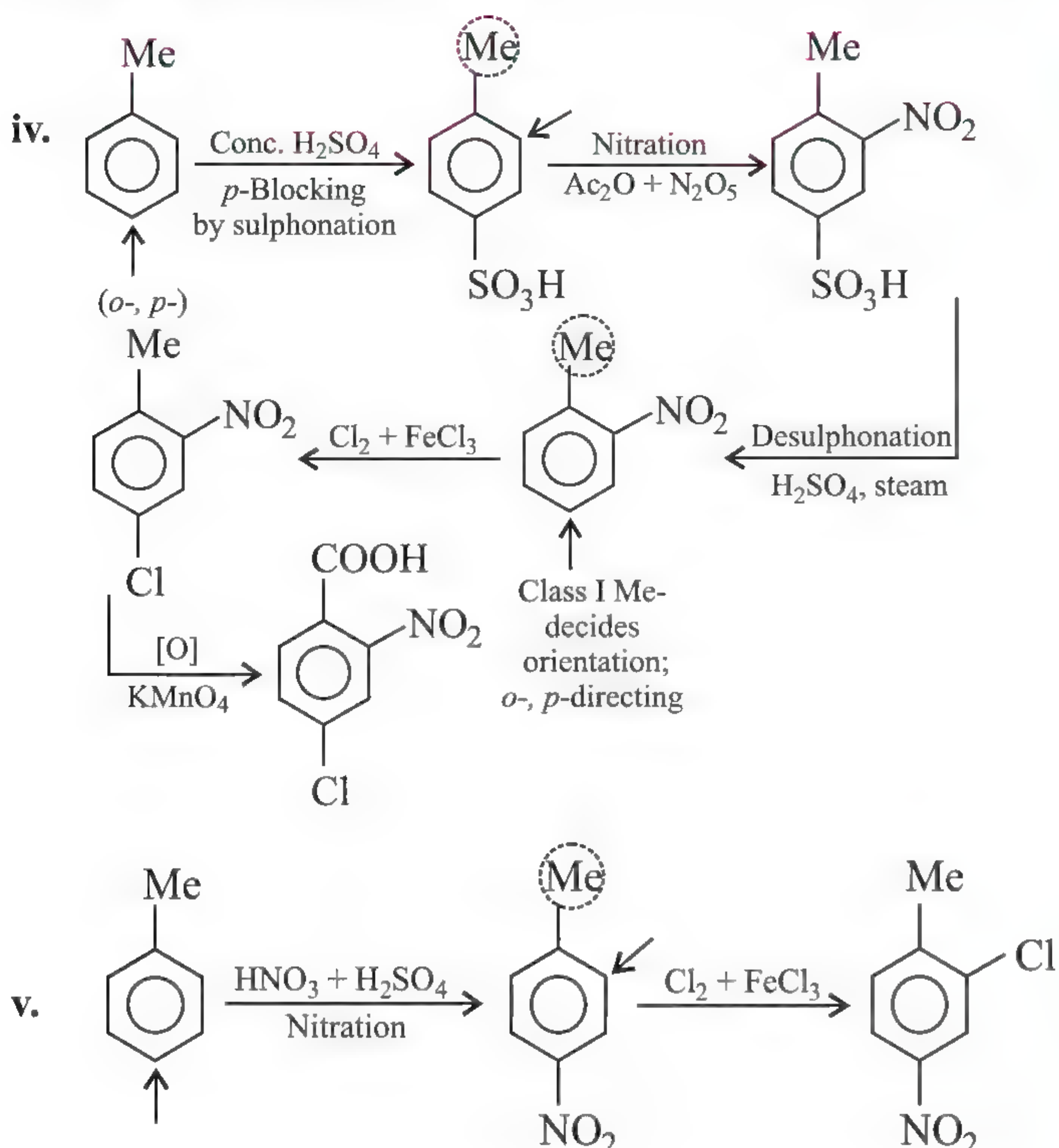
ILLUSTRATION 3.20

Convert the following:



Sol.

To get mainly *ortho*-isomer, *p*-position is blocked first by sulphonation.iii. First, introduce *m*-directing ($-\text{NO}_2$) group and then proceed with bromination.



vi. First, convert (Me) group to *m*-directing ($-\text{COOH}$) or (CCl_3) group, then after introducing ($-\text{Cl}$) group convert ($-\text{COOH}$) or (CCl_3) to (Me).

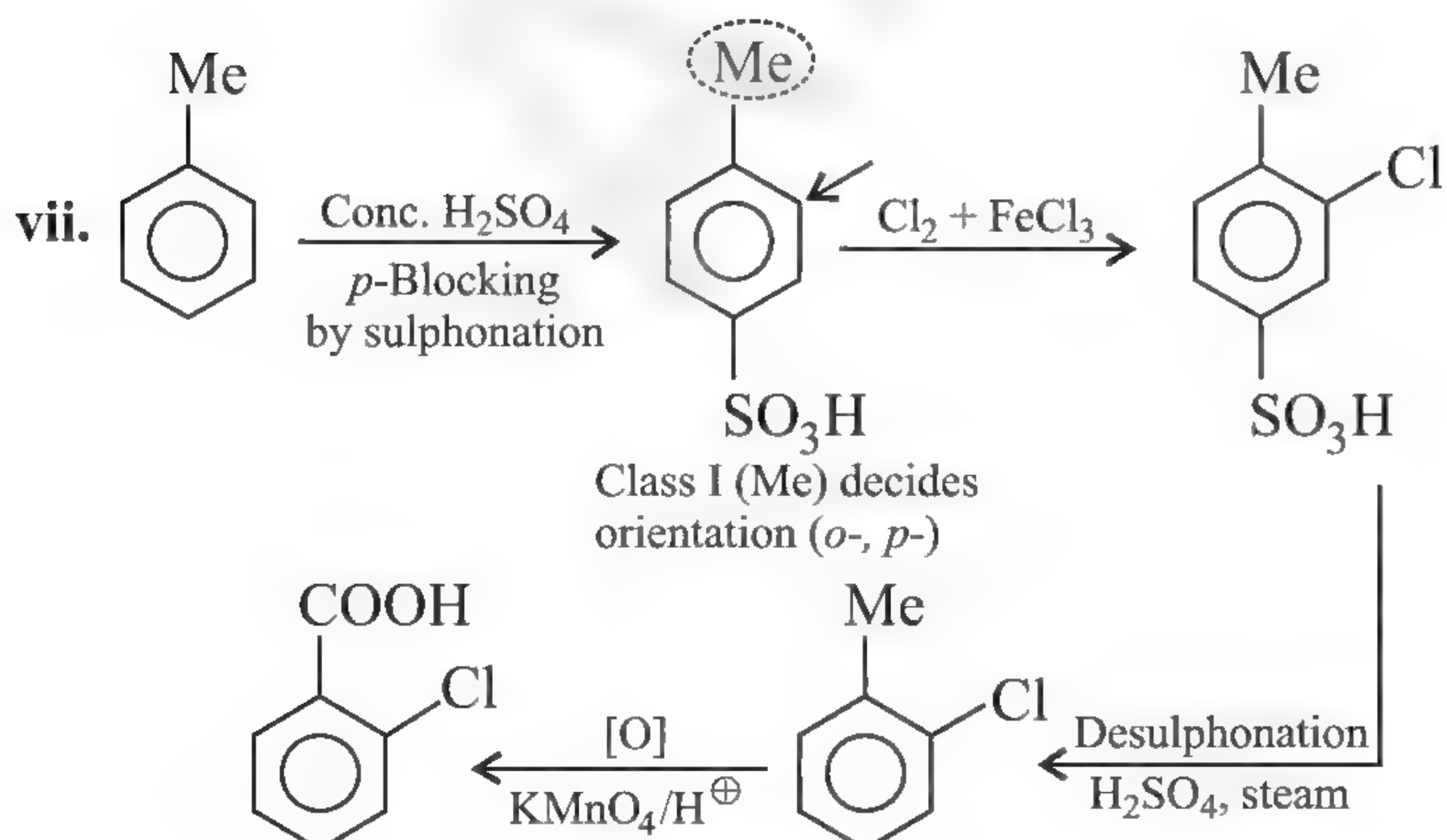
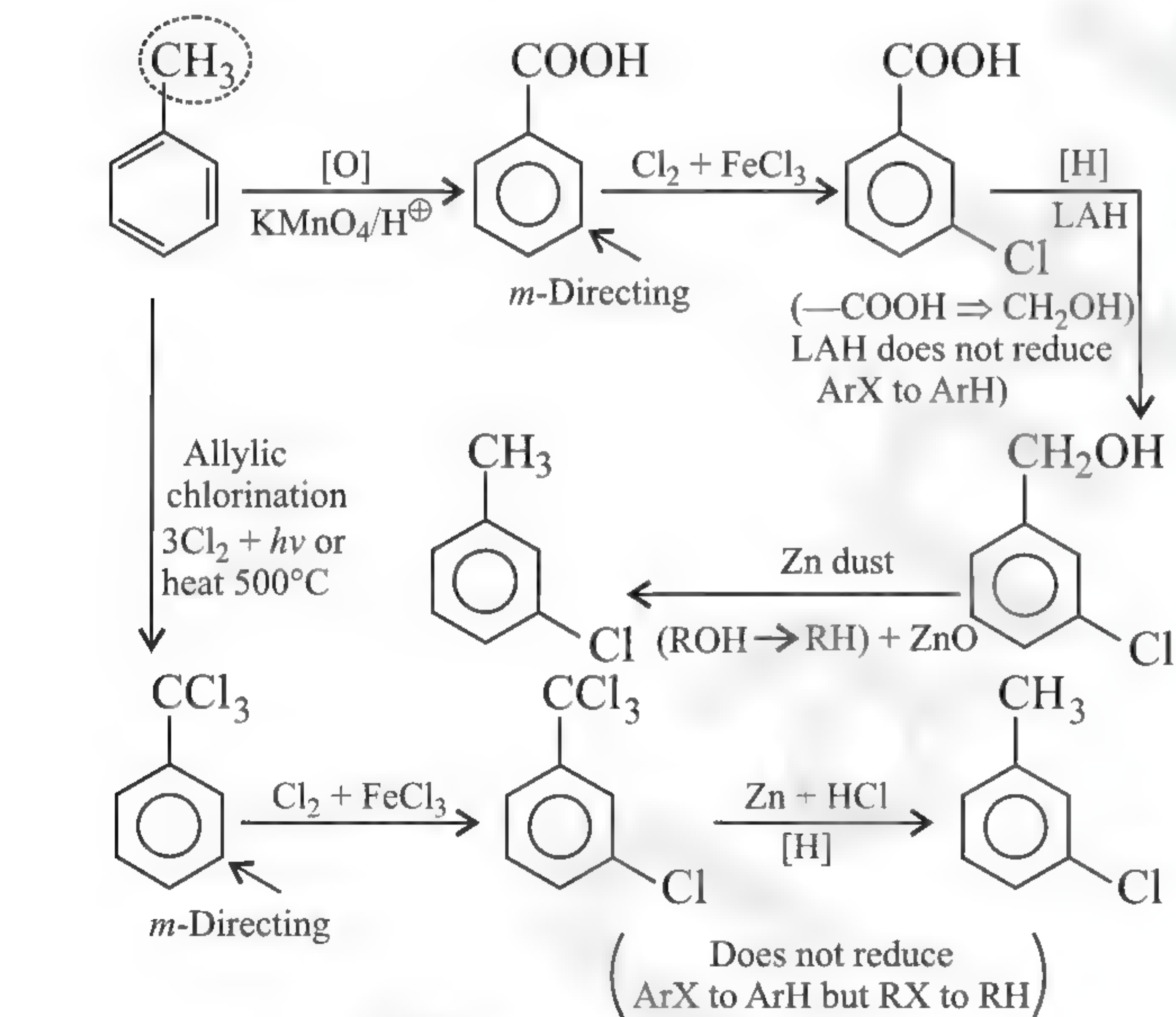
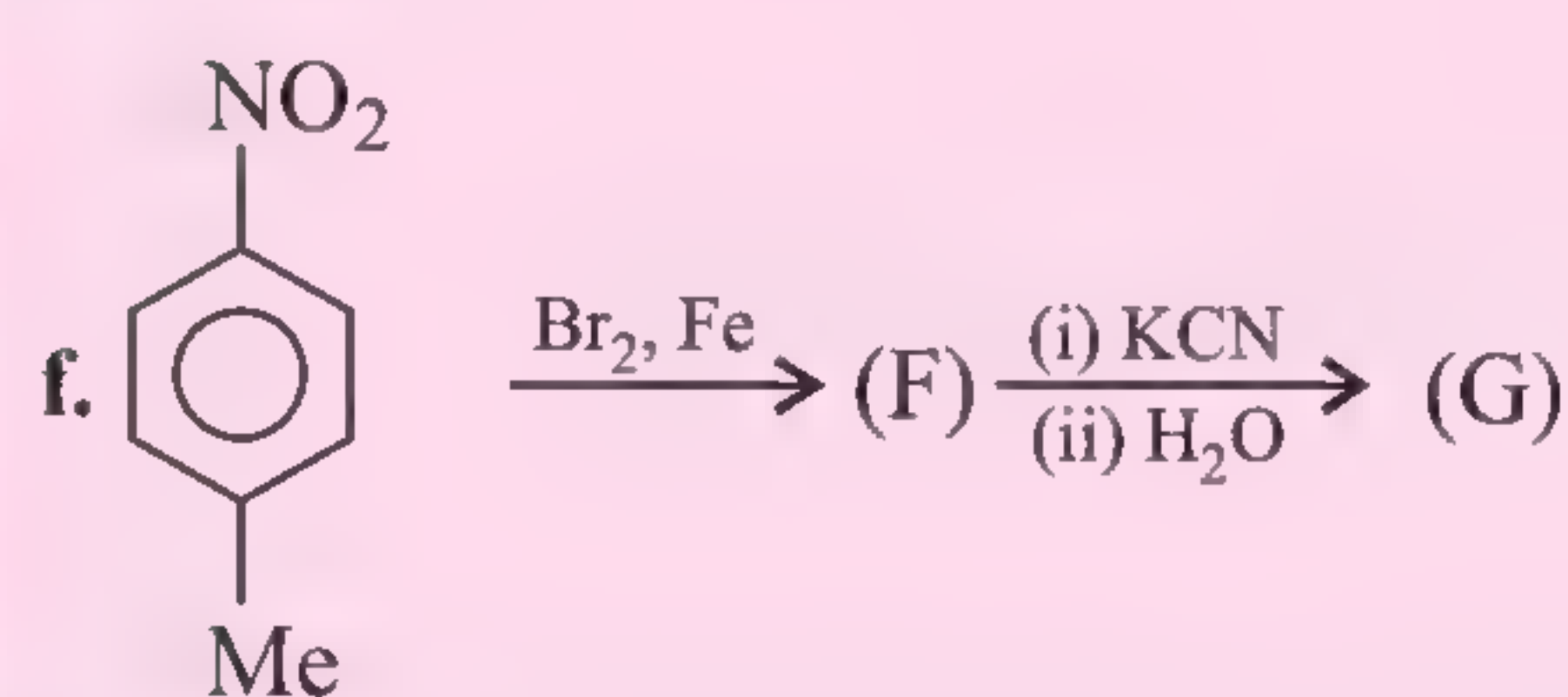
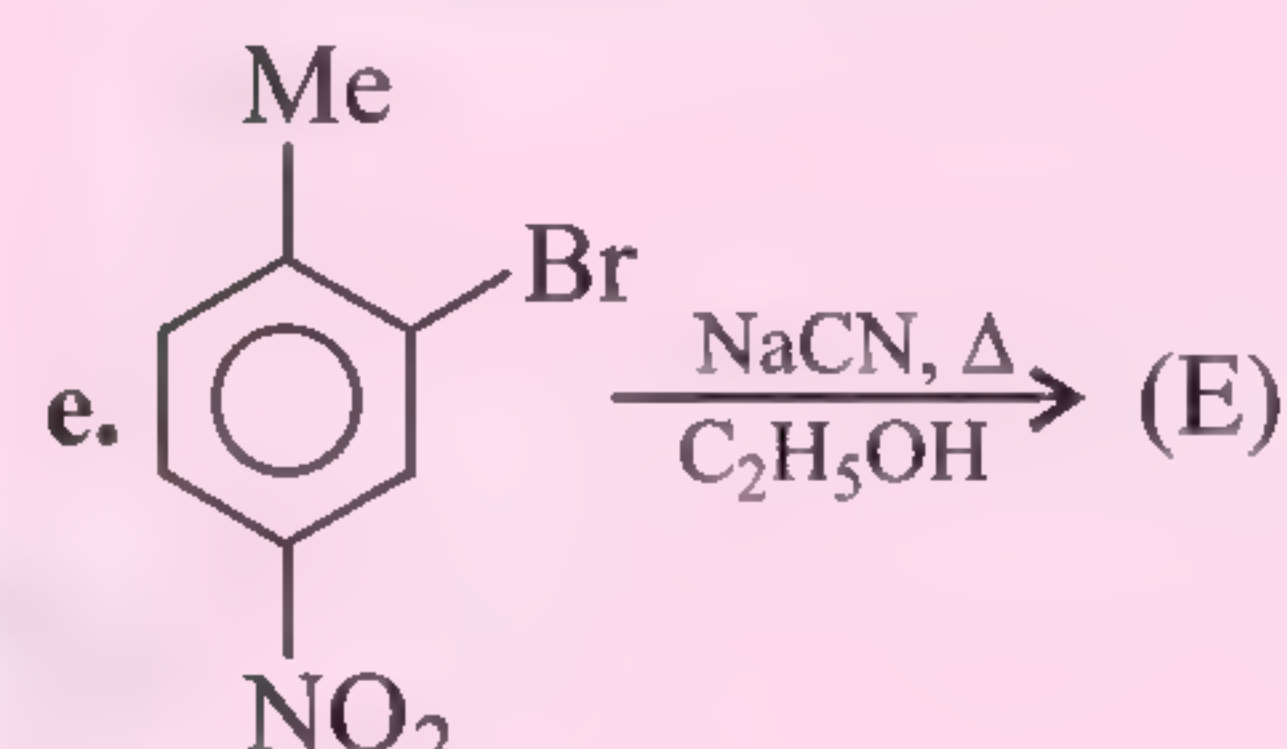
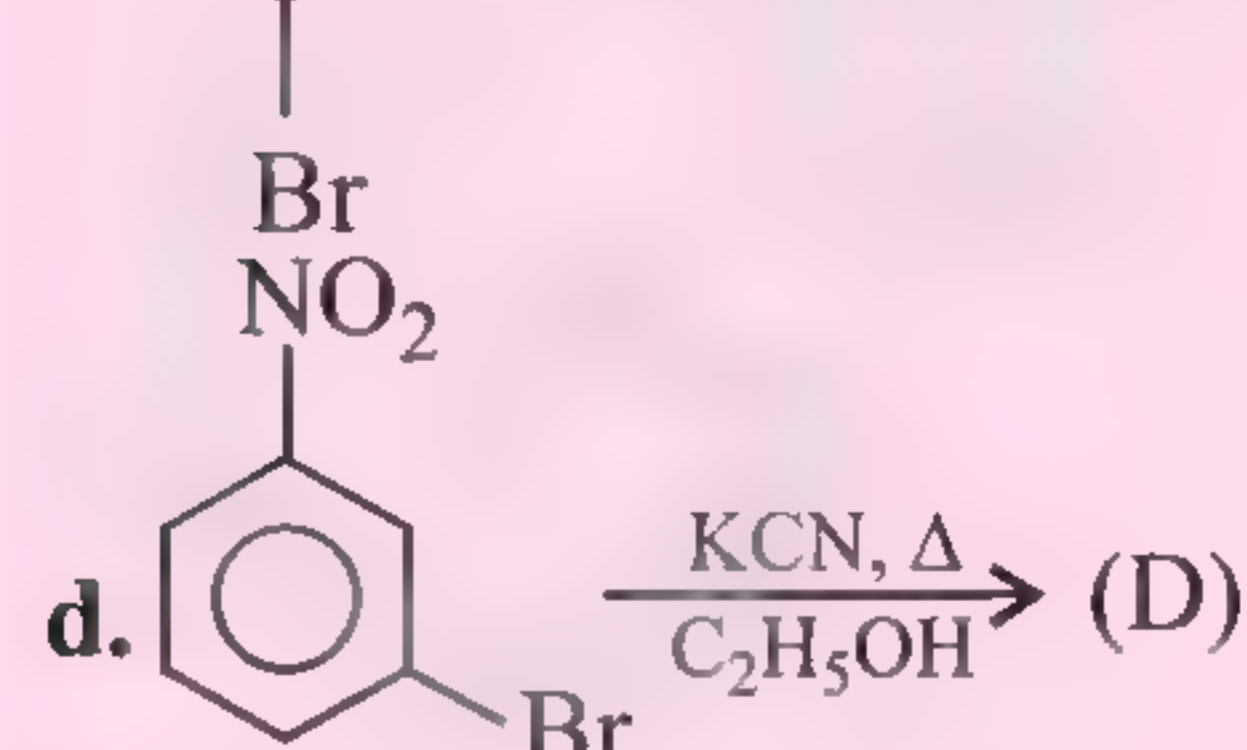
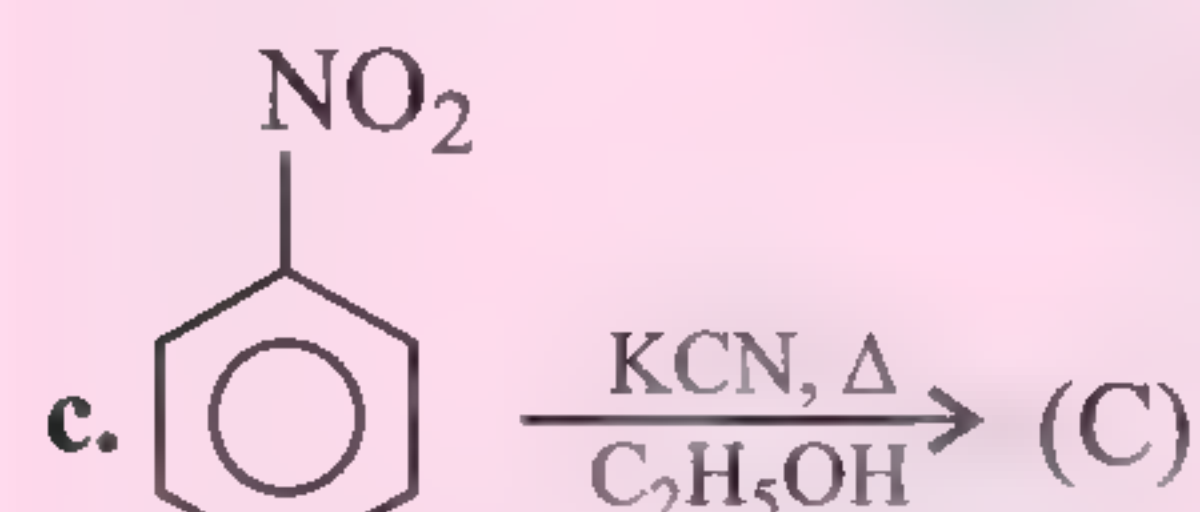
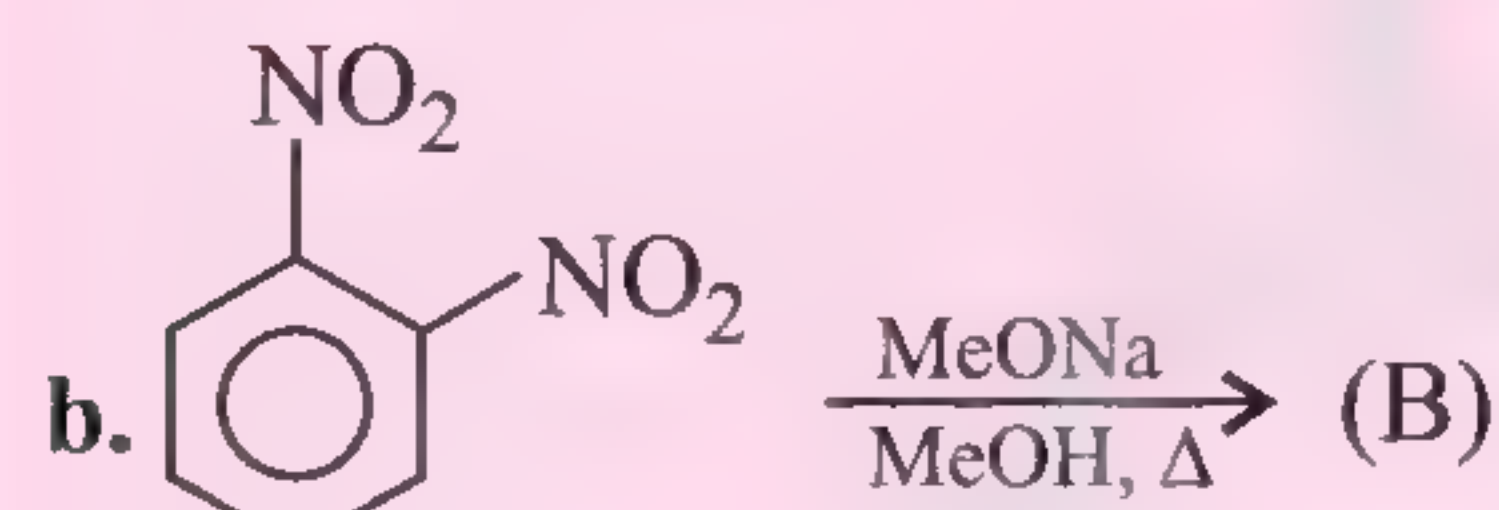
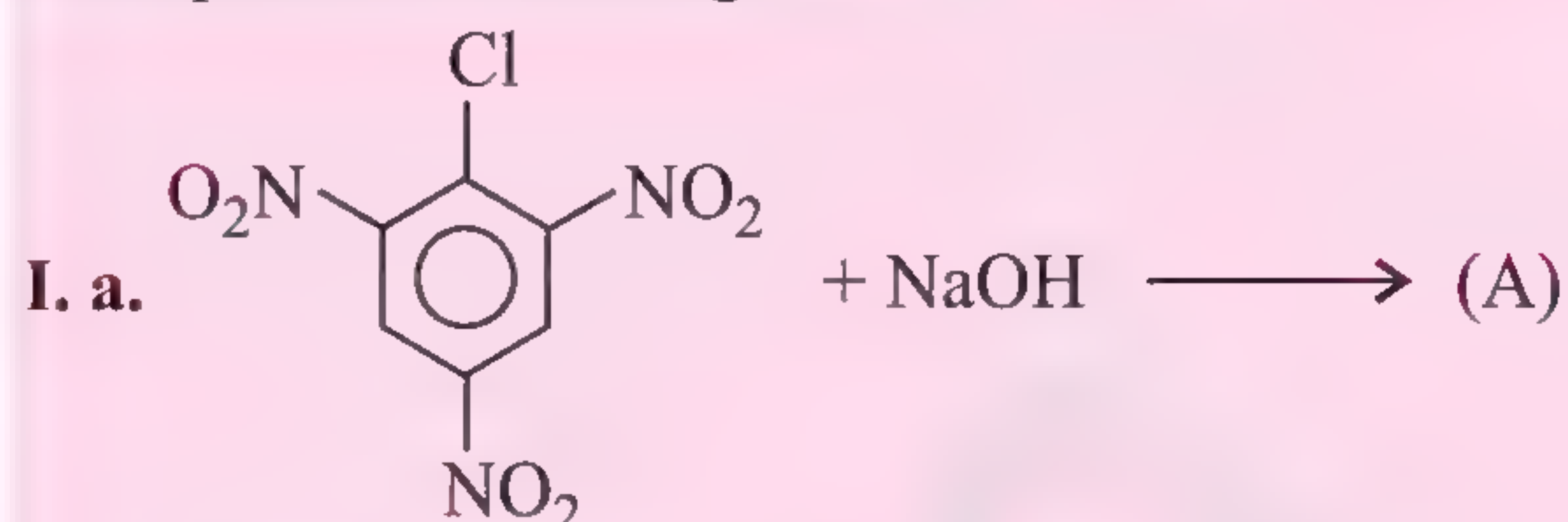
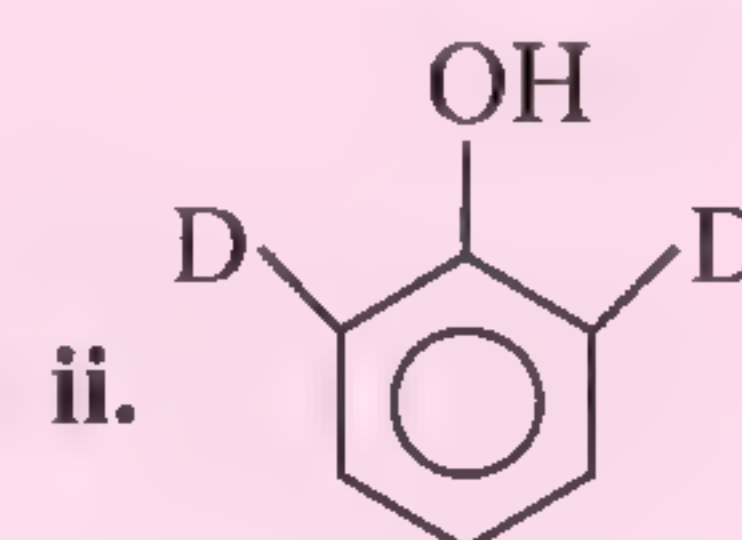
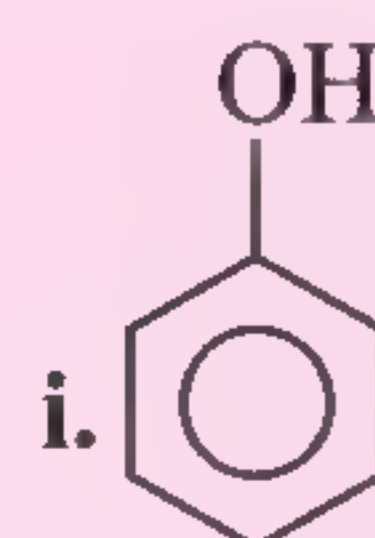


ILLUSTRATION 3.21

Complete the following:



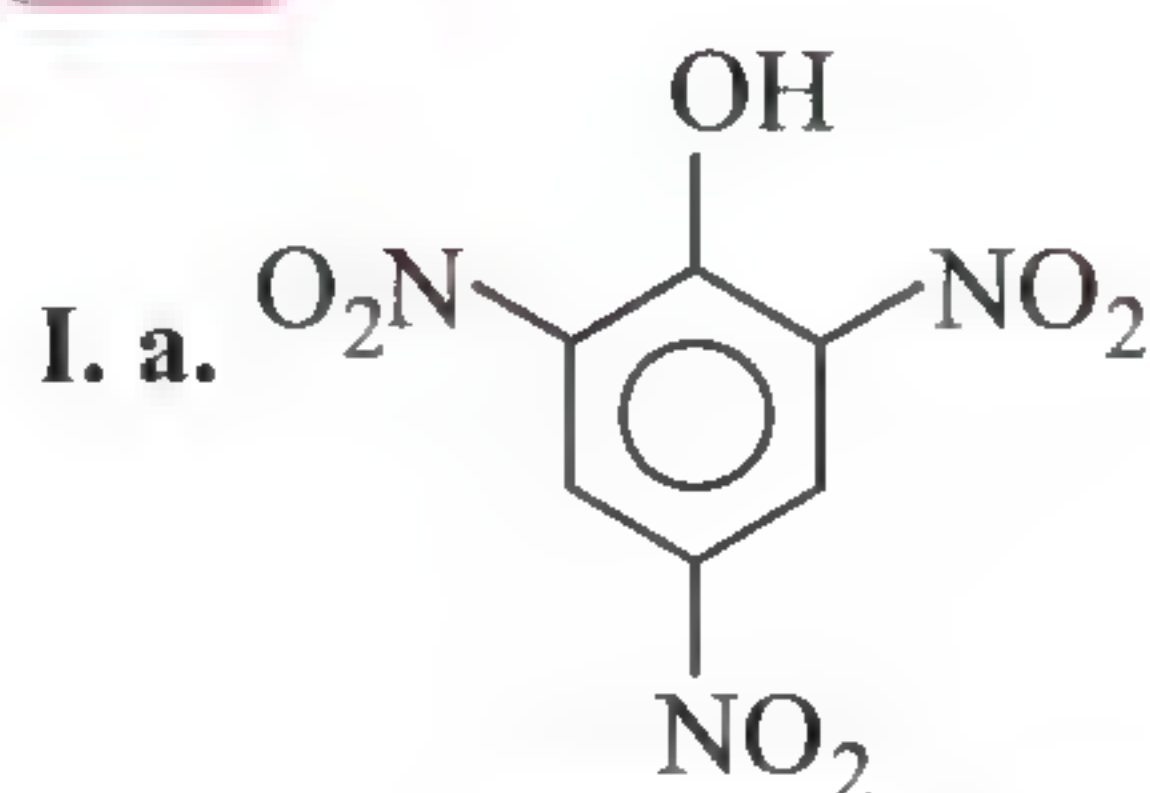
II. Which of the following has the greater K_a value?



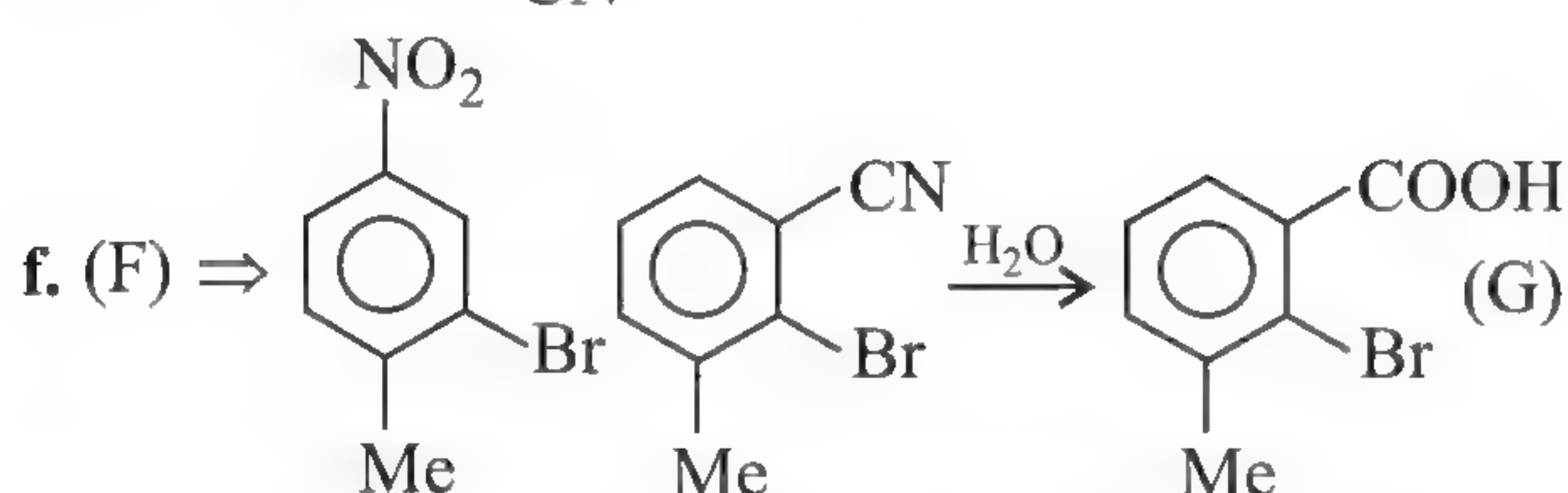
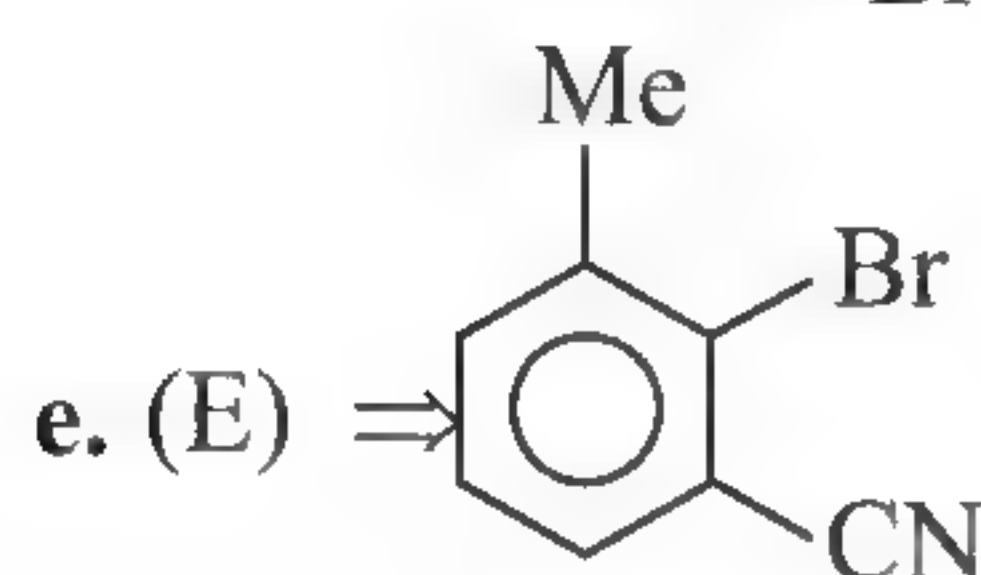
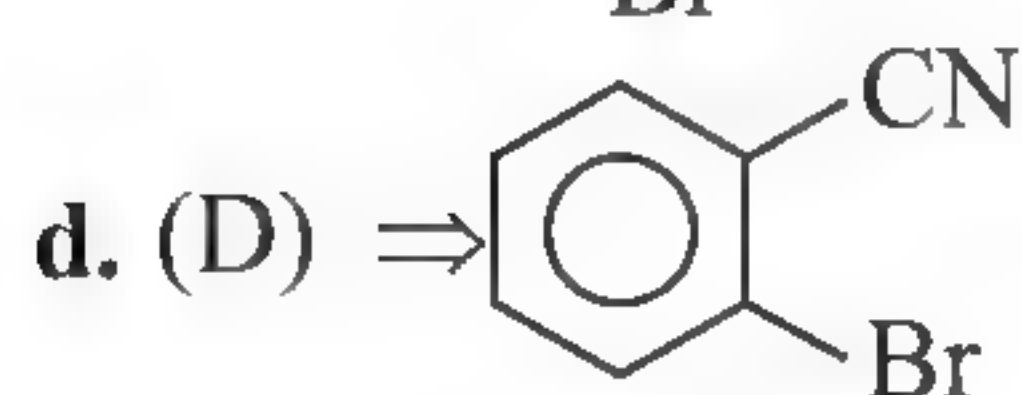
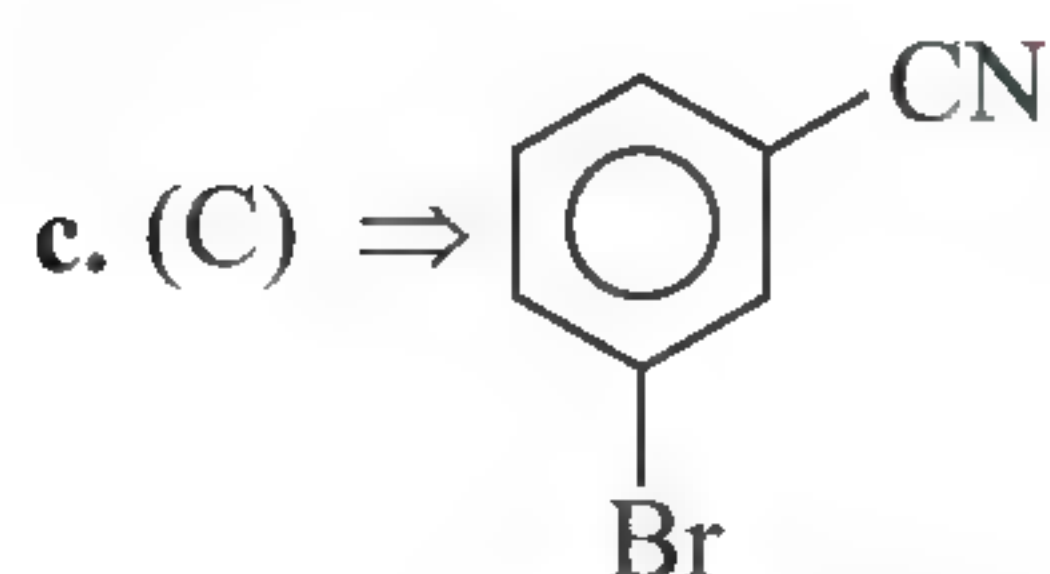
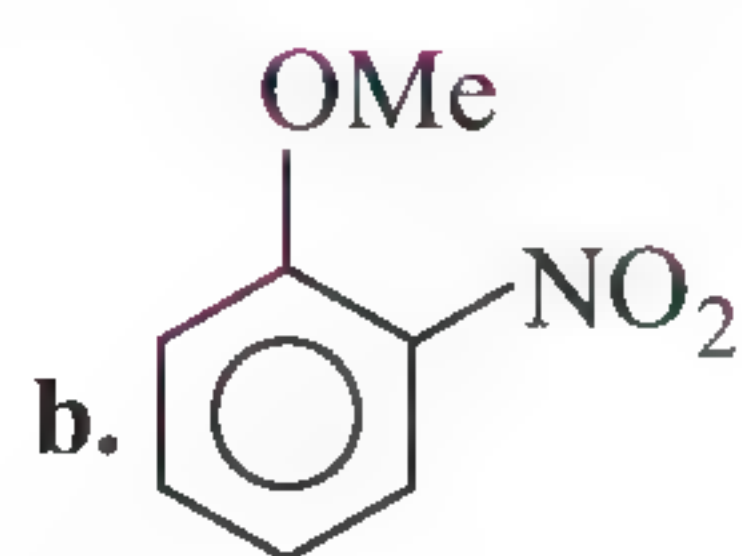
III. Which of the carbonyl groups in (a) and (b) protonate more readily in acid solution and why?



Sol.

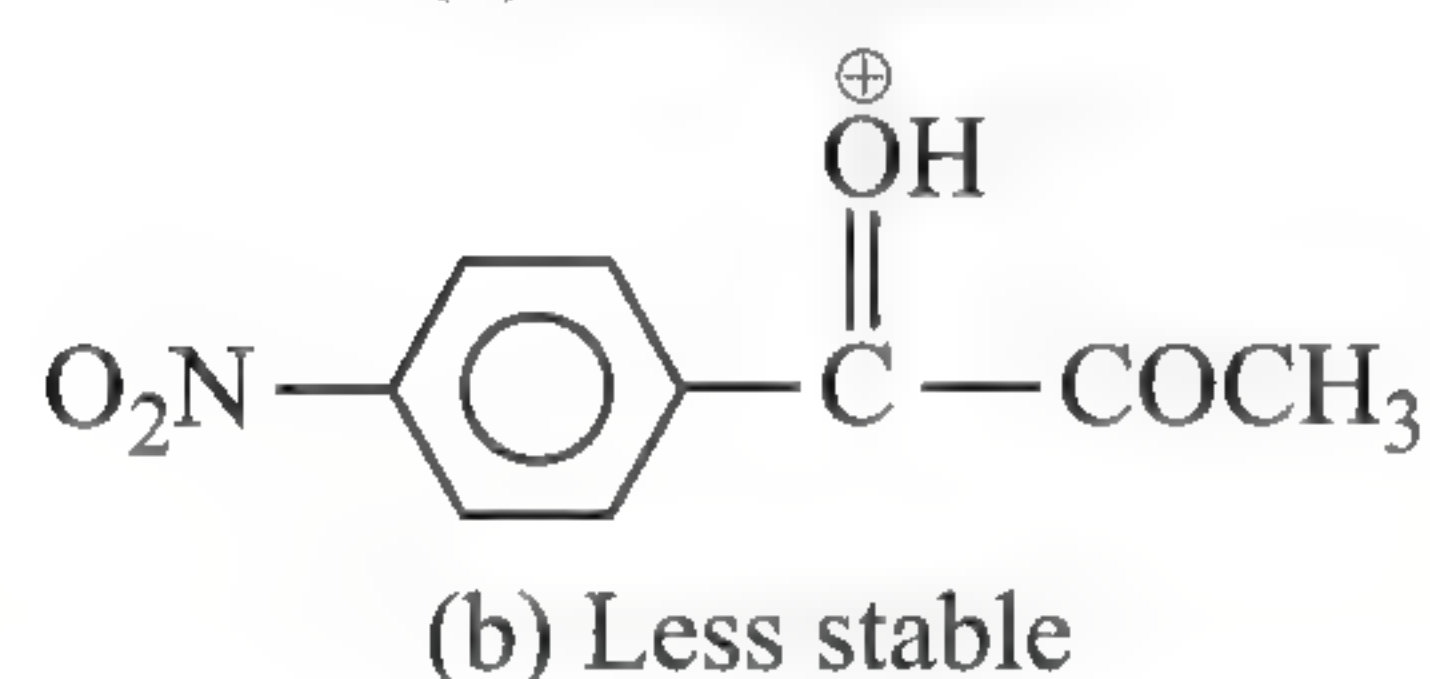
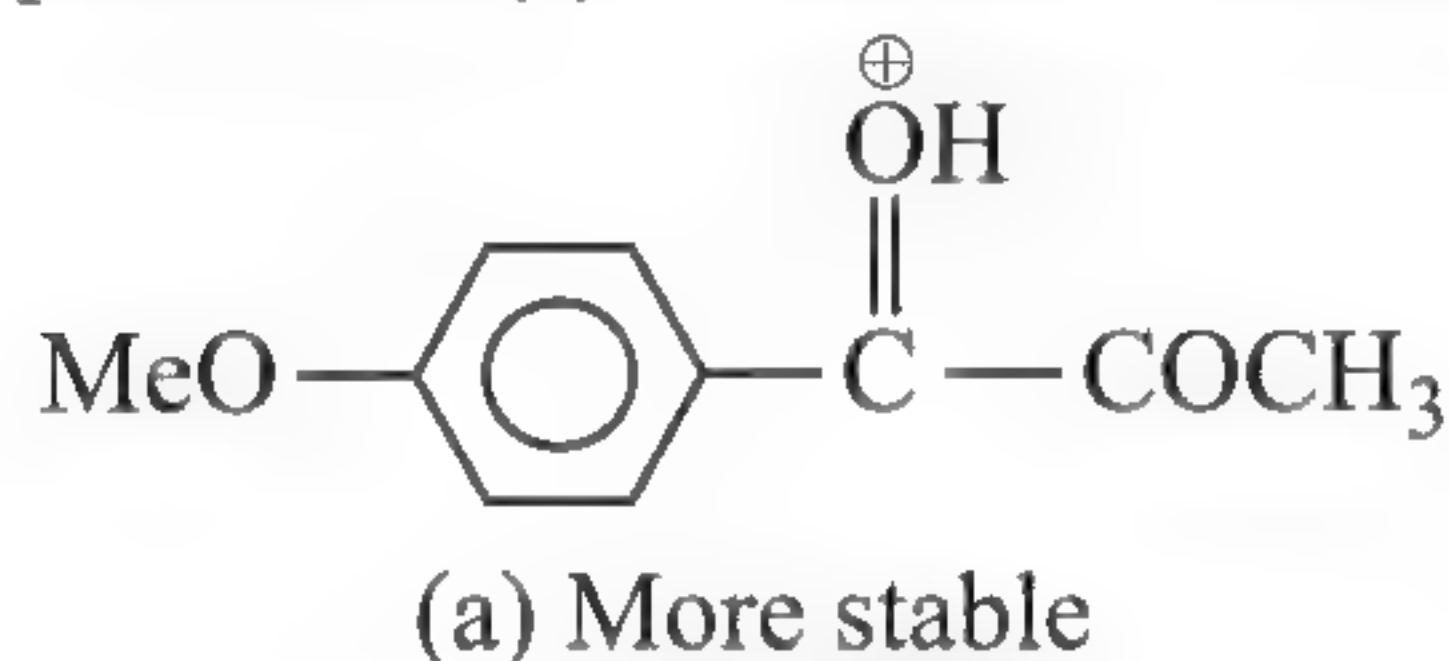


[Due to three \bar{e} -withdrawing (NO_2) groups ($\text{C}-\text{Cl}$) bond is weakened.]



II. Deuterium is more \bar{e} -donating than H atom. Hence K_a of (i) > (ii).

III. Protonation of (a) takes place more readily than (b), since protonated (a) is more resonance stabilised than protonated (b).

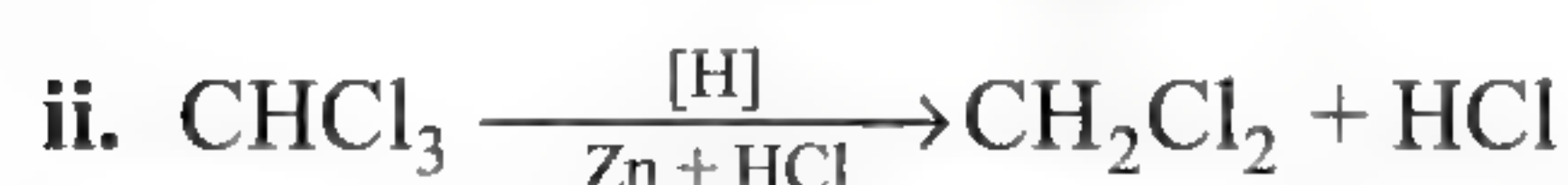
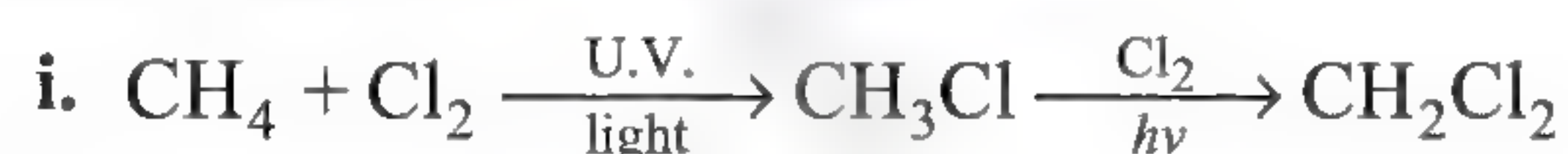


3.20 POLYHALOGEN COMPOUNDS

Carbon compounds containing more than one halogen are called polyhalogen compounds.

3.20.1 METHYLENE CHLORIDE OR DICHLOROMETHANE (CH_2Cl_2)

a. It is prepared by the direct chlorination of methane. The mixture so obtained is separated by fractional distillation. It can be prepared by partial reduction of CHCl_3 with metal and acid ($\text{Zn} + \text{HCl}$).



It is a colourless, sweet smelling, volatile liquid, with a boiling point of 313 K. Because of its low boiling point and low inflammability, it is an effective extraction solvent used in pharmaceutical and food industries. It is widely used as:

- Solvent
- Paint remover

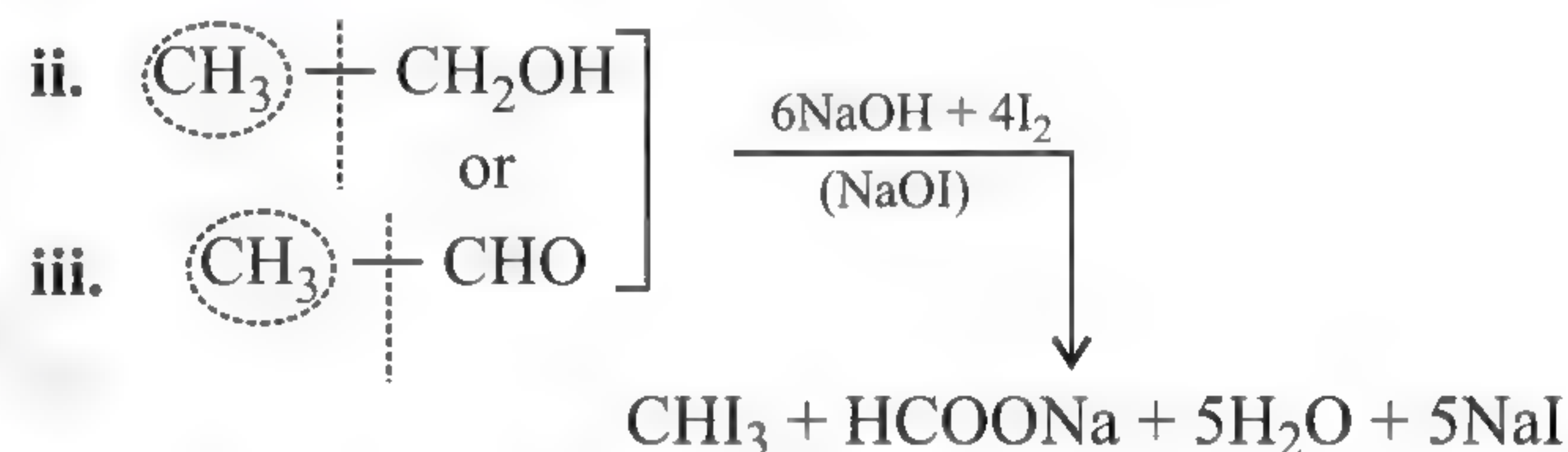
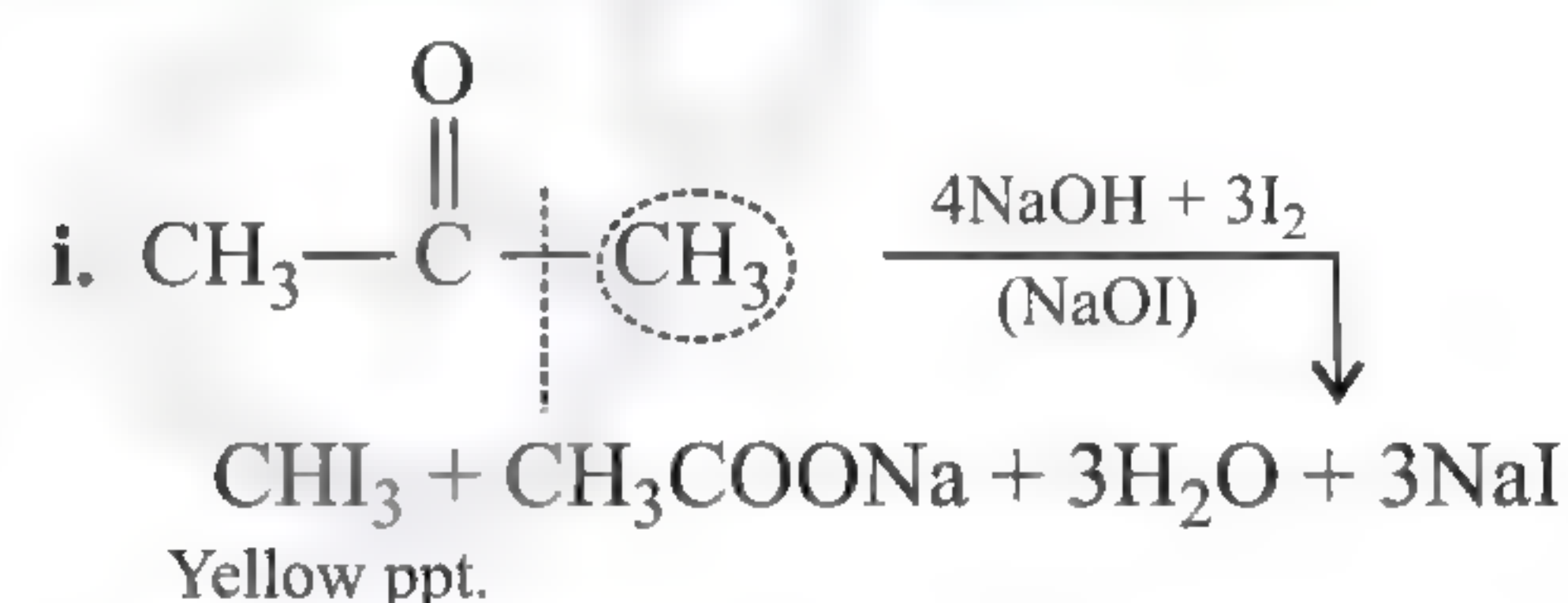
- Propellant in aerosols
- Metal cleaning and finishing solvent
- Process solvent in the manufacturing of drugs

b. Harmful effects:

- It harms human central nervous system (CNS).
- It leads to slightly impaired hearing and vision on exposure to lower levels of CH_2Cl_2 in air.
- It causes dizziness, nausea, tingling, and numbness in the fingers and toes on exposure to higher levels of CH_2Cl_2 in air.
- Direct human skin contact with CH_2Cl_2 causes intense burning sensation and mild redness of the skin. Direct contact with eyes can burn the cornea.

3.20.2 TRIIDO METHANE (IODOFORM) (CHI_3)

It can be prepared by iodoform reaction.



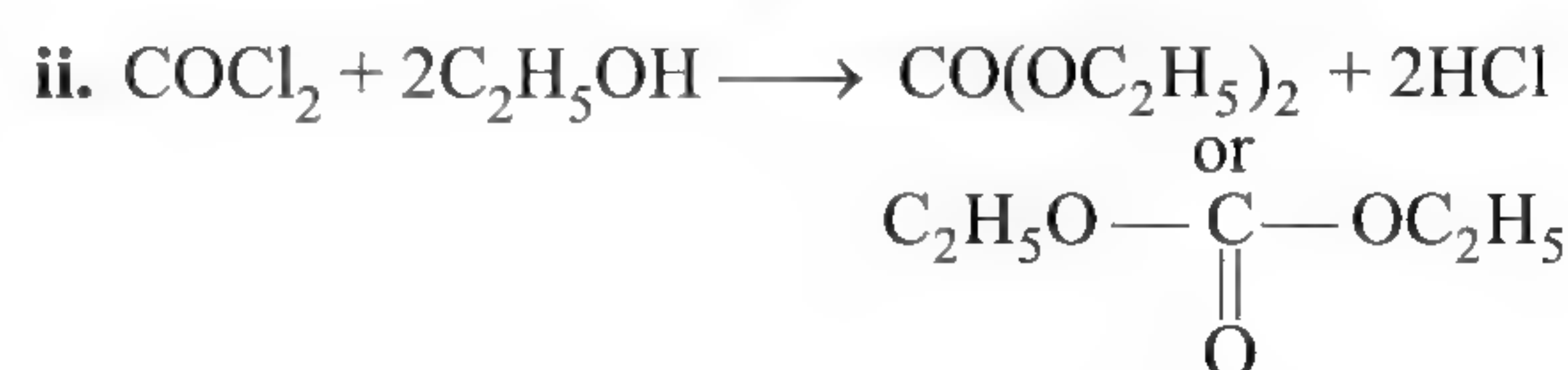
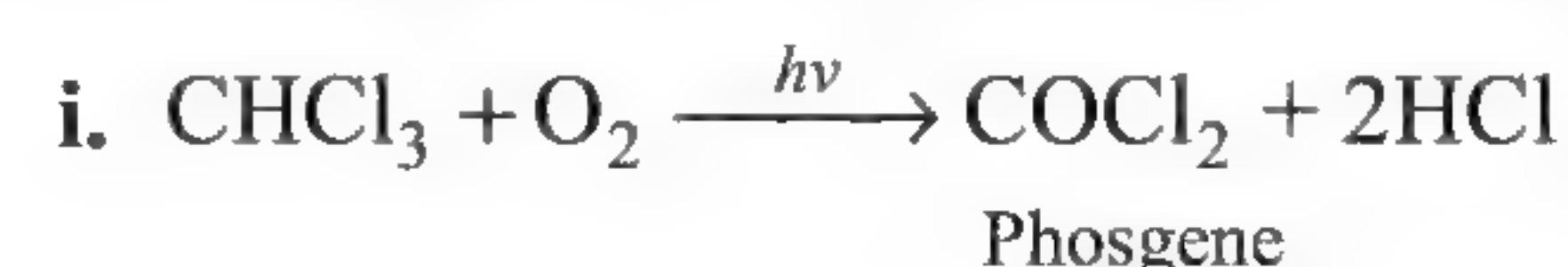
It was used as an antiseptic but the antiseptic properties are due to the liberation of free I_2 and not due to iodoform itself. It has been replaced with other compounds containing iodine due to its objectionable smell.

3.20.3 CHLOROFORM OR TRICHLOROMETHANE (CHCl_3)

It is used in the manufacture of freon refrigerant R-22 ($\text{C}_2\text{F}_2\text{Cl}_4$). Inhaling CHCl_3 vapours depresses the CNS. Inhaling of 900 ppm for a short time can cause dizziness, fatigue, and headache. Chronic CHCl_3 exposure may cause damage to liver (where CHCl_3 is metabolised to phosgene) and kidneys, and some people develop sores when skin is immersed in CHCl_3 . It was widely used as an anaesthetic because of its toxic nature, but it is no longer in use.

It is manufactured by chlorination of methane and the mixture is separated by fractional distillation. It is a sweet smelling, colourless liquid, immiscible with water but miscible with organic solvents, and is a good solvent for oils, fats, waxes, alkaloids, and iodine.

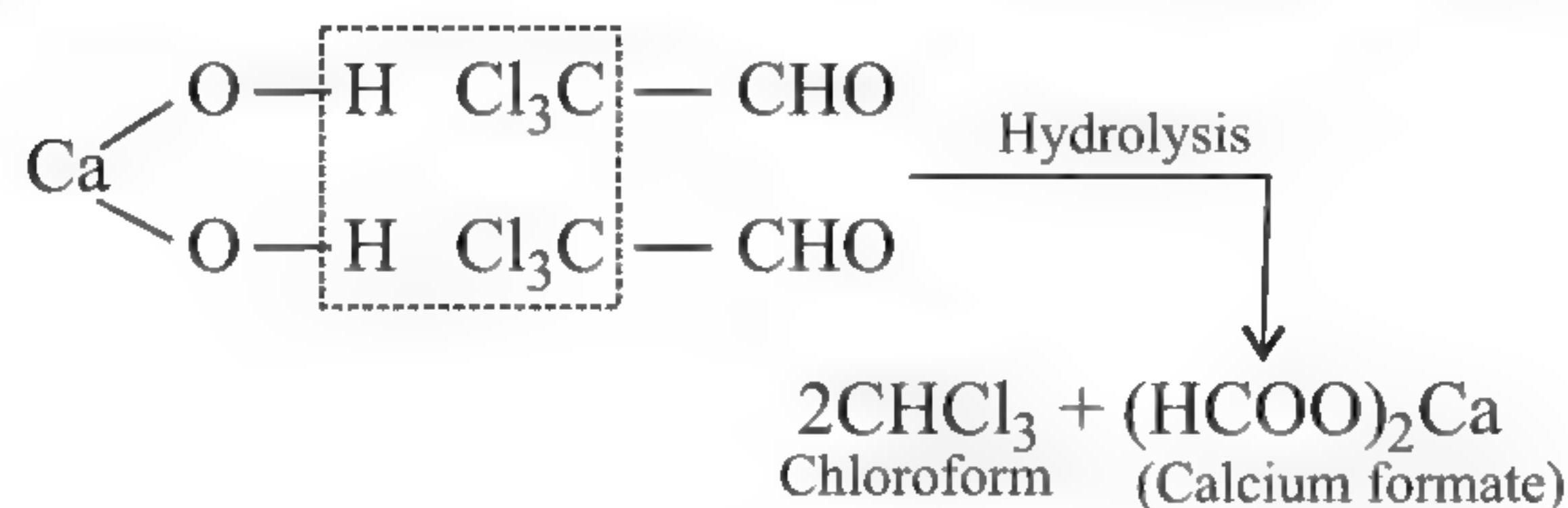
It is slowly oxidised by air in the presence of light to a poisonous gas, phosgene (carbonyl chloride). It is therefore stored in coloured bottles, completely filled, so that air is kept out. Addition of little ethanol converts the toxic phosgene to harmless diethyl carbonate.



(a) Preparation:

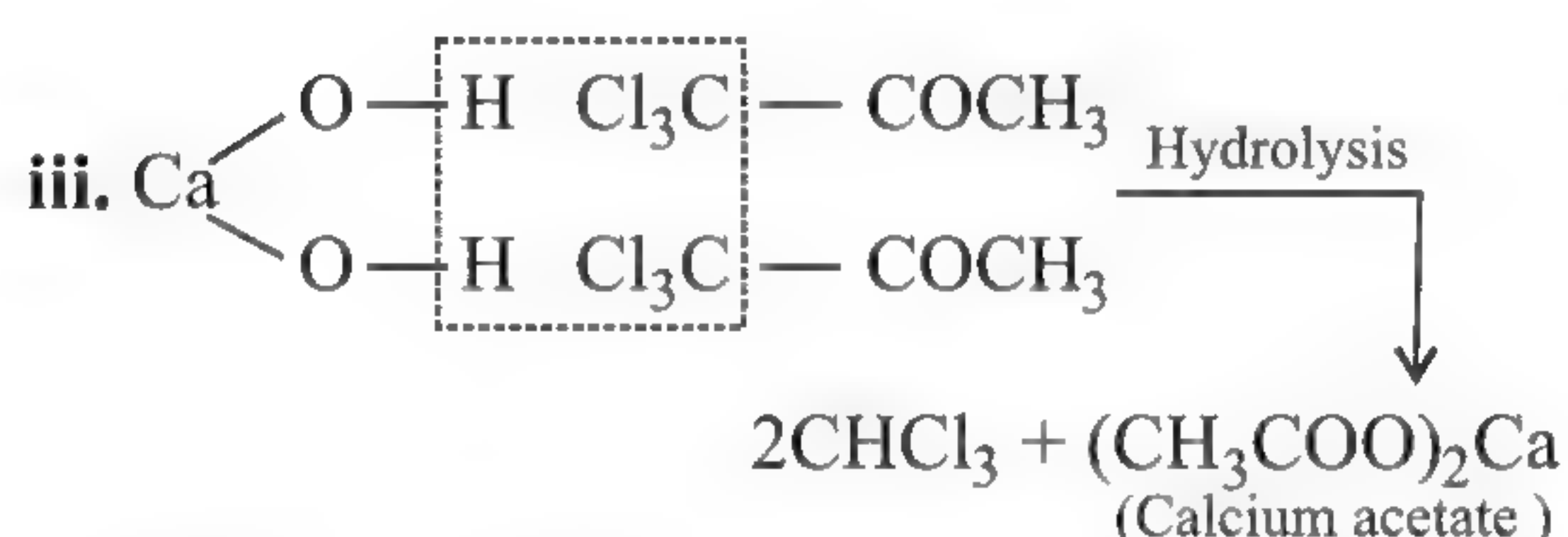
It is prepared by distilling ethanol or acetone with a suspension of bleaching powder in water (laboratory method), e.g.

- i. $\text{CaOCl}_2 + \text{H}_2\text{O} \longrightarrow \text{Cl}_2 + \text{Ca(OH)}_2$
- ii. $\text{CH}_3\text{CH}_2\text{OH} + \text{Cl}_2 \xrightarrow{\text{Oxid.}} \text{CH}_3\text{CHO} + 3\text{HCl}$
- iii. $\text{CH}_3\text{CHO} + 3\text{Cl}_2 \xrightarrow[\text{Chlorination}]{\text{Ca(OH)}_2} \text{Cl}_3\text{C}-\text{CHO} + 3\text{HCl}$
- iv. Chloral is then hydrolysed by Ca(OH)_2 to give CHCl_3 .



In case of acetone, the reactions are:

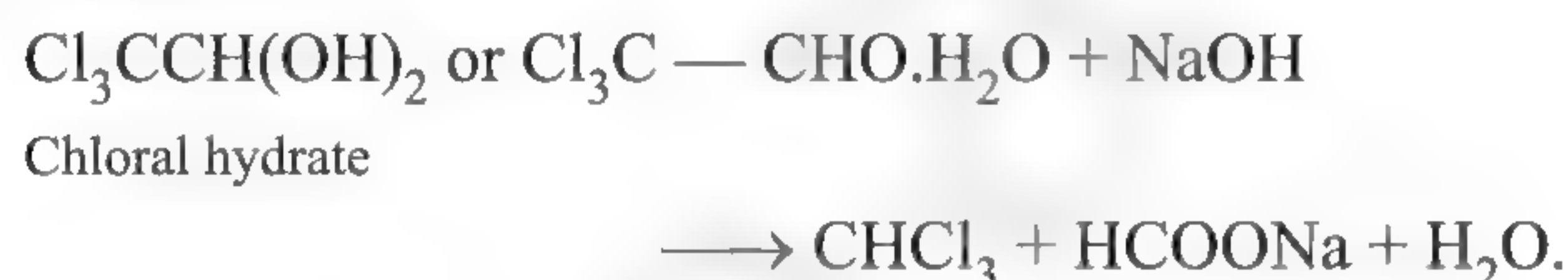
- i. $\text{CaOCl}_2 + \text{H}_2\text{O} \longrightarrow \text{Cl}_2 + \text{Ca(OH)}_2$
- ii. $\text{CH}_3\text{COCH}_3 + 3\text{Cl}_2 \xrightarrow[\text{Chlorination}]{\text{Ca(OH)}_2}$
 $\text{Cl}_3\text{C}-\overset{1}{\text{C}}-\overset{2}{\text{CO}}-\overset{3}{\text{CH}_3} + \text{HCl}$
1,1,1-Trichloro propan-2-one



Acetone is preferred to ethanol as the yield is better. In place of bleaching powder, an alkaline solution of sodium hypochlorite (NaOCl) may be used.

- i. $2\text{NaOH} + \text{Cl}_2 \text{ (Cold)} \longrightarrow \text{NaOCl} + \text{NaCl} + \text{H}_2\text{O}$
- ii. $\text{CH}_3\text{COCH}_3 + 3\text{NaOCl} \longrightarrow \text{CH}_3\text{COCCL}_3 + \text{NaOH}$
- iii. $\text{CH}_3\text{CO}[\text{CCl}_3 + \text{H}] \text{ONa} \longrightarrow \text{CHCl}_3 + \text{CH}_3\text{COONa}$

Pure chloroform may be obtained by the action of NaOH on chloral hydrate.

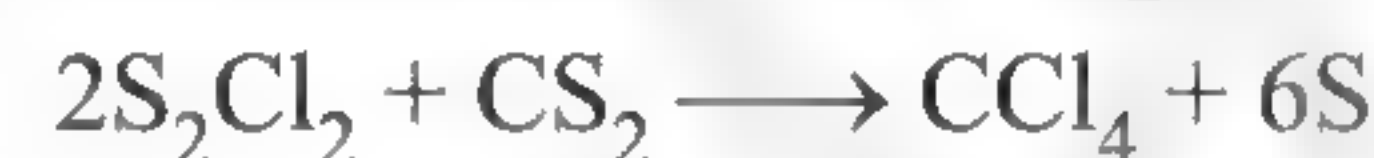
**(b) Reactions:**

- i. $\text{CHCl}_3 + 2[\text{H}] \xrightarrow{\text{Zn} + \text{HCl}} \text{CH}_2\text{Cl}_2 \text{ (Methylene chloride)} + \text{HCl}$
- ii. $\text{CHCl}_3 + 6[\text{H}] \xrightarrow{\text{Zn dust} + \text{H}_2\text{O}} \text{CH}_4 + 3\text{HCl}$
- iii. $\text{CHCl}_3 + \text{Cl}_2 \xrightarrow{\text{Sunlight}} \text{CCl}_4 + \text{HCl}$
- iv. $\text{HCCl}_3 \xrightarrow[-3\text{KCl}]{+3\text{KOH}} [\text{HC(OH)}_3] \xrightarrow{-\text{H}_2\text{O}} [\text{HCOOH}]$
 $\xrightarrow[\text{-H}_2\text{O}]{\text{KOH}} \text{HCOOK (Pot. formate)}$
- v. $\text{HC}[\text{Cl}_3 + 6\text{Ag} + \text{Cl}_3]\text{CH} \xrightarrow{\Delta} \text{CH} \equiv \text{CH} + 6\text{AgCl}$
Acetylene
- vi. $\text{CHCl}_3 + \text{HNO}_3 \longrightarrow \text{Cl}_3\text{NO}_2 + \text{H}_2\text{O}$
Chloropicrin
(Used as tear gas)

3.20.4 CARBON TETRACHLORIDE (OR TETRACHLOROMETHANE) (CCl_4)

- i. $\text{CH}_4 + 4\text{Cl}_2 \xrightarrow{\text{CuCl}_2} \text{CCl}_4 + 4\text{HCl}$
- ii. $\text{CS}_2 + 3\text{Cl}_2 \xrightarrow[\text{or FeCl}_3]{\text{AlCl}_3} \text{CCl}_4 + \text{S}_2\text{Cl}_2$
(Sulphur monochloride)

S_2Cl_2 , formed in the process, is separated by fractional distillation and then treated with CS_2 to yield more CCl_4 .



It is a colourless, volatile, non-inflammable liquid, used as a fire extinguisher under the name **pyrene**. It is insoluble in H_2O and soluble in organic solvents.

(a) Reactions

- i. $\text{CCl}_4 + \text{H}_2\text{O} \longrightarrow \text{COCl}_2 \text{ (Phosgene)} + 2\text{HCl}$
- ii. $\text{CCl}_4 + 2[\text{H}] \xrightarrow{\text{Fe/H}_2\text{O}} \text{CHCl}_3 + \text{HCl}$
- iii. $\text{CCl}_4 + 4\text{KOH} \xrightarrow[-4\text{KCl}]{\Delta} [\text{C(OH)}_4] \downarrow$
 $\text{CO}_2 + 2\text{H}_2\text{O}$



- iv. $3\text{CCl}_4 + 2\text{SbF}_3 \xrightarrow{\text{SbCl}_5} 3\text{CCl}_2\text{F}_2 \text{ (Freon-12)} + 2\text{SbCl}_3$

(b) Uses:

- i. Used in the manufacture of refrigerants and propellants for aerosol cans.
- ii. Used in the synthesis of CFCs (chloro fluorocarbons) and other chemicals and in pharmaceutical manufacturing.
- iii. Used as a cleaning solvent (dry cleaning), and as a degreasing agent, as a spot remover, and as fire extinguisher (pyrene).

(c) Harmful effects:

- i. It causes dizziness, light-headedness, nausea, vomiting which can cause permanent damage to nerve cells. Subsequently, these effects may lead to stupor, coma, unconsciousness, or death.
- ii. Exposure to CCl_4 may cause irregular heart beat or heart failure. It may irritate the eyes on contact.
- iii. In air, it depletes the ozone layer which increases the level of ultraviolet rays, causing skin cancer, eye diseases, and disruption of the human immune system.

3.21 FREONS

- a. The chlorofluorocarbon (CFC) compounds of CH_4 and C_2H_6 are known as freons. They are stable, non-toxic, non-corrosive, unreactive, and easily liquefiable gases. Freon-12 is widely used.

b. Nomenclature of Freon:

Freon-12: The first number (e.g., 1) denotes C atom, whereas the second number (e.g., 2) denotes the number of F atoms and the remaining H atoms in CH_4 or C_2H_6 are replaced by Cl atoms. Number of Cl atoms is not mentioned.

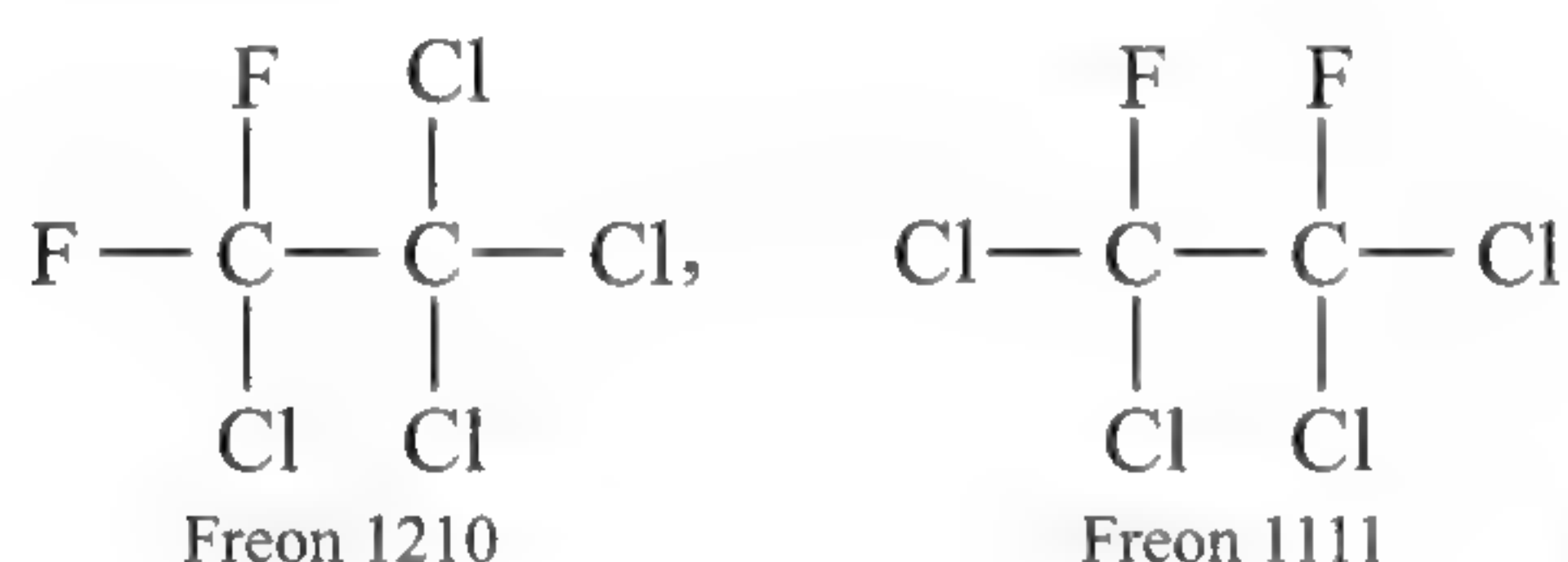
Freon-22 (These are obtained from ethane, since it contains two C atoms).

Alkane

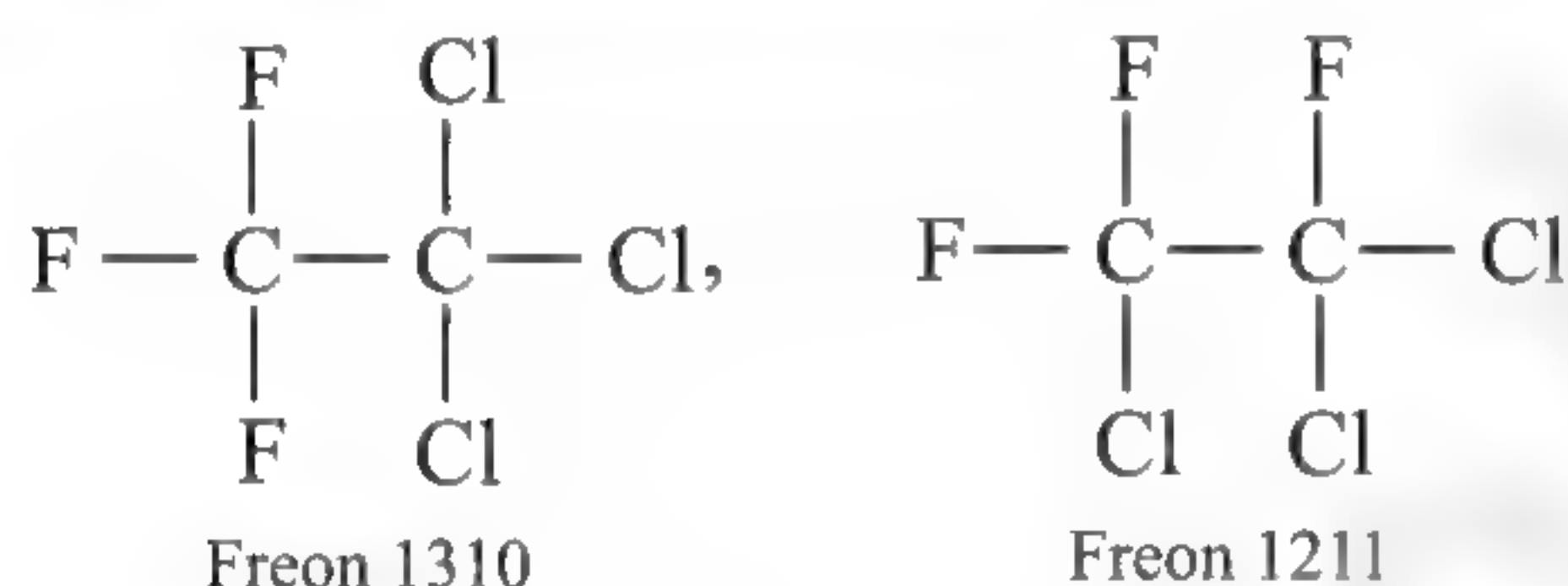
CH ₄	Freon-11 CFCl ₃ (1 C, 1 F, 3 Cl)
	Freon-12 CF ₂ Cl ₂ (1 C, 2 F, remaining H atoms are replaced by 2 Cl atoms)
	Freon-13 CF ₃ Cl (1 C, 3 F, 1 Cl)
C ₂ H ₆	Freon-22 C ₂ F ₂ Cl ₄ (2 C, 2 F, remaining 4 H atoms replaced by Cl atoms)
	Freon-23 C ₂ F ₃ Cl ₃ (2 C, 3 F, 3 Cl)
	Freon-24 C ₂ F ₄ Cl ₂ (2 C, 4 F, 2 Cl)

Freon derived from ethane can exist in various isomeric forms and the numerals are written according to the number of C and F atoms.

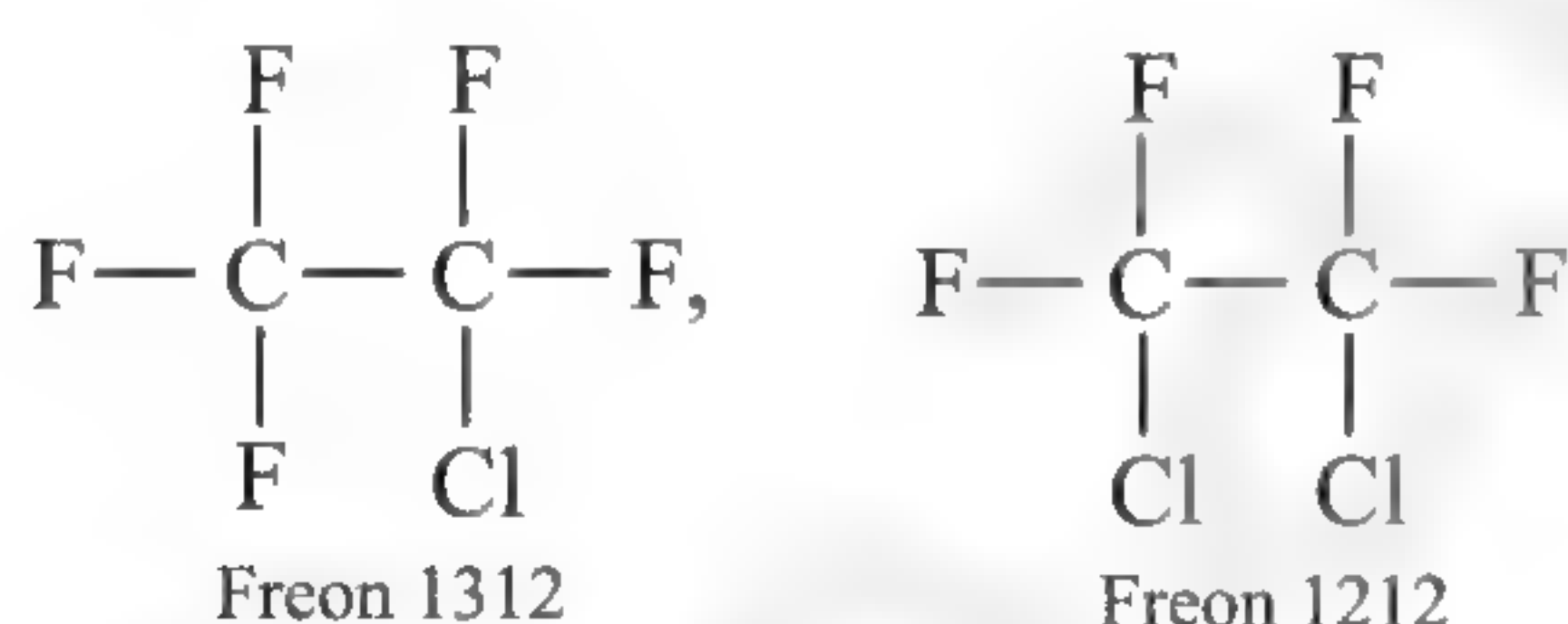
Freon-22 (C₂F₂Cl₄) can exist as:



Freon-23 (C₂F₃Cl₃) can exist as:



Freon-24 (C₂F₄Cl₂) can exist as:



- c. **Preparation:** Freon-12 is prepared from CCl₄ by Swarts reactions.



- d. **Uses:** Freons are used as refrigerants, as propellants in aerosols and foams (i.e., hair spray, deodorants, etc.).

Its use as propellants in aerosols has been banned in the USA since these are responsible for the depletion of the ozone layer.

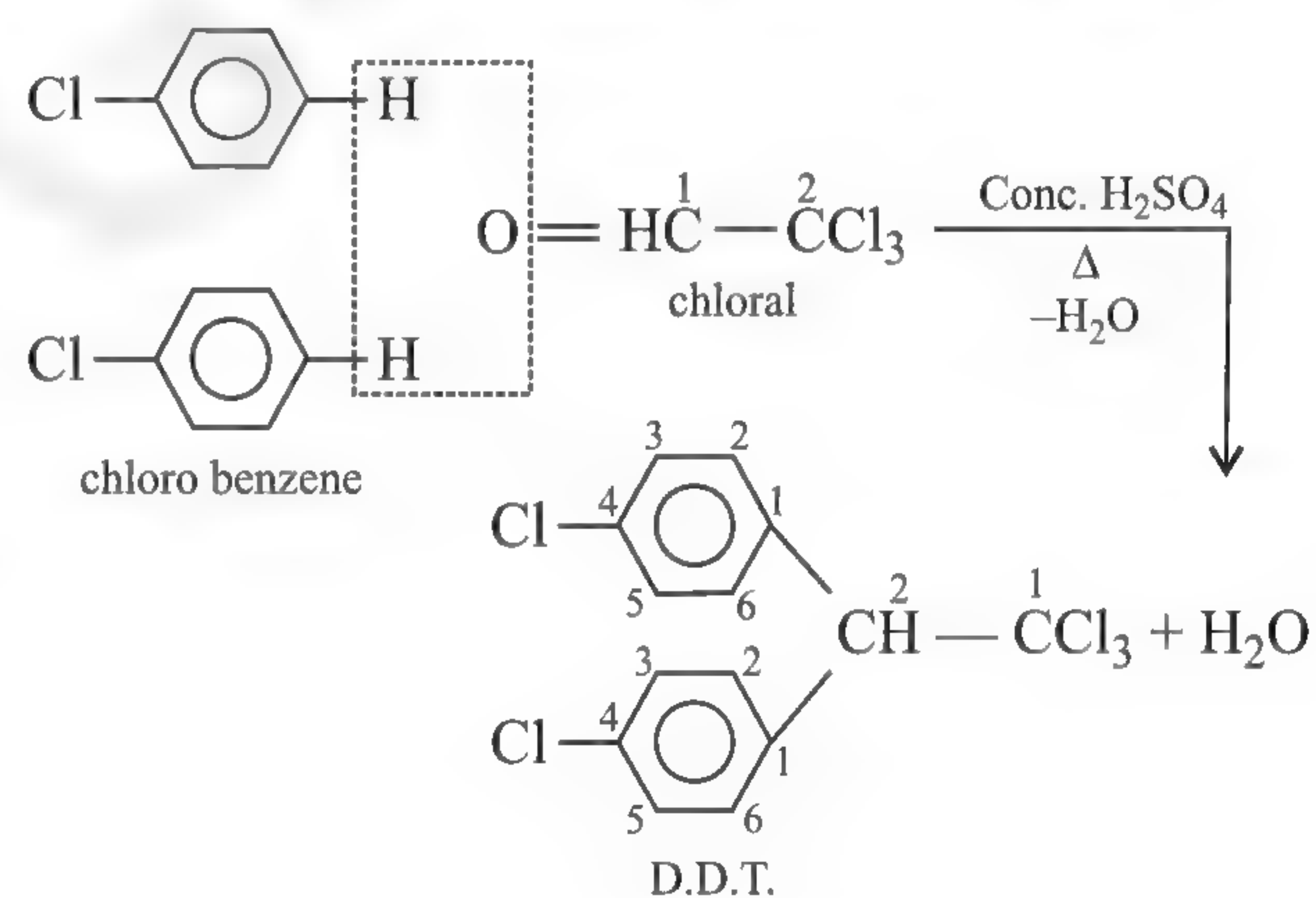
These compounds remain in the atmosphere for years and eventually enter its upper layer where they get broken down by the U.V. radiation emitted by the sun. The life time of (CFC-12)(CF₂Cl₂) is 139 years, while that for (CFC-11) (CFCl₃) is 77 years. The decomposition products of CFCs destroy the ozone by initiating the radical chain reaction.



These Cl atoms are free to react with more O₃. Many O₃ molecules can thus be destroyed for each of the Cl atom produced. One Cl atom can destroy 1000 O₃ molecules.

3.22 D.D.T. (p,p'-DICHLORODIPHENYL TRICHLORO-ETHANE)

- a. **IUPAC name:** 2,2-bis(4-chlorophenyl)-1,1,1-trichloroethane.
- b. **Preparation:** It is prepared by heating chloral (trichloro acetaldehyde or 2,2,2-trichloroethanal) with two moles of chlorobenzene in the presence of concentrated H₂SO₄.

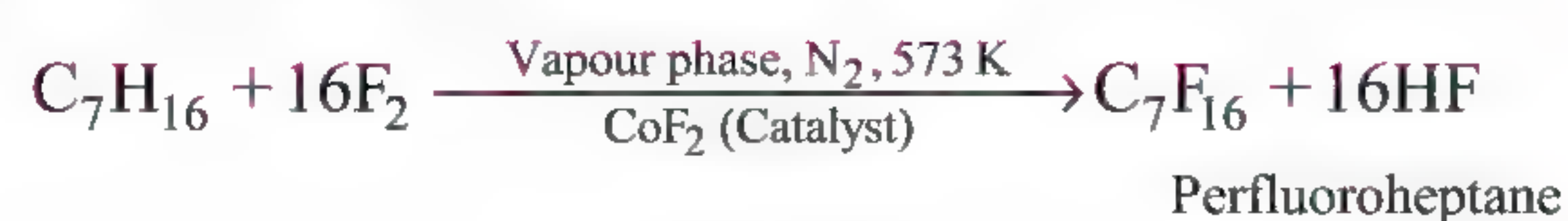


D.D.T., the first chlorinated organic insecticide, was prepared in 1873. But its effectiveness as an insecticide was discovered in 1939 by Paul Muller of Geigy Pharmaceuticals in Switzerland. In 1948, Paul Muller was awarded the Nobel Prize in medicine and physiology.

- c. **Uses:** It is a cheap but powerful insecticide for mosquitoes that spread malaria and lice that carry typhus.
- d. **Harmful effects:** Due to its extensive use since 1940s, many species of insects developed resistance to D.D.T. It has high toxicity towards fish. Due to its stability and fat solubility, it is not metabolised rapidly by animals but is deposited and stored in the fatty tissues. It was banned in the USA in 1973, but is still used in many parts of the world due to the non-availability of any other better and cheaper insecticides.

3.23 PERFLUOROCARBONS (PFCS)

- a. Perfluorocarbons (C_nF_{2n+2}) are obtained by controlled fluorination of vaporised alkanes diluted with nitrogen gas in the presence of a catalyst.



- b. Perfluorocarbons are colourless, odourless, non-toxic, non-corrosive, non-polar, extremely stable, and unreactive gases, liquids, or solids. They are stable to ultraviolet light and other ionising radiations and, therefore, do not deplete the ozone layer. They are good electrical insulators and are used as lubricants, surface coatings, dielectrics, heat transfer media in high-voltage electrical equipment, etc. In electronic industry, they are used for phase soldering, gross leak detection of sealed micro-chips, etc. They find several applications in healthcare and medicine, e.g., in skincare cosmetics, wound healing, liquid ventilation, retina reattachment, carbon monoxide poisoning, and medical diagnosis.

CONCEPT APPLICATION EXERCISE 3.1

1. On disulphonation followed by fusion with NaOH and acidification, an aromatic compound C_8H_{10} (A) gives two isomeric compounds (B) and (C) (molecular formula $\text{C}_8\text{H}_{10}\text{O}_2$). Oxidation of esters of (B) and (C) followed by hydrolysis gives two isomeric compounds (D) and (E) ($\text{C}_7\text{H}_6\text{O}_4$), which may be decarboxylated to form $\text{C}_6\text{H}_6\text{O}_2$ (F). Identify compounds (A) to (F).
2. An organic compound $\text{C}_6\text{H}_4\text{O}_2\text{NCl}$ (A) reacts with alkali to give $\text{C}_6\text{H}_5\text{O}_3\text{N}$ (B). On reduction with tin and HCl, (B) gives $\text{C}_6\text{H}_7\text{ON}$ (C), whereas on milder reduction it gives (D) $\text{C}_6\text{H}_7\text{O}_2\text{N}$, which rearranges in the presence of a mineral acid to give a new compound (E). Identify the various compounds from (A) to (E).
3. A hydrocarbon C_9H_{10} (A) rapidly decolourises cold aqueous permanganate and rapidly absorbs one molecule of bromine. Vigorous hydrogenation of (A) gives a compound (B) of the formula C_9H_{18} . Strong oxidation of (A) yields phthalic acid. Propose a structure for (A) and give the basis for your answer.

19. Fluorobenzene (C_6H_5F) can be synthesised in the laboratory:

- (1) By heating phenol with HF and KF.
- (2) From aniline by diazotisation followed by heating the diazonium salt with HBF_4 .
- (3) By direct fluorination of benzene with F_2 gas.
- (4) By reacting PhBr with NaF solution.

20. Bottles containing PhI and $PhCH_2I$ lost their original labels. They were labelled as (A) and (B) for testing. (A) and (B) were separately taken in test tubes and boiled with NaOH solutions. The end solution in each tube was made acidic with dilute HNO_3 and some $AgNO_3$ solution was added. Substance (B) gave a yellow precipitate. Which of the following statements is true for this experiment?

- (1) Addition of HNO_3 was unnecessary
- (2) (A) was PhI
- (3) (A) was $PhCH_2I$
- (4) (B) was PhI

21. Phenol can be converted to 1, 3, 5-tribromo benzene by using the sequence

- (1) Br_2/H_2O
- (2) (i) Br_2/H_2O (ii) Zn-dust
- (3) (i) Br_2/CS_2 (ii) Zn-dust
- (4) (i) Zn-dust (ii) Br_2/H_2O

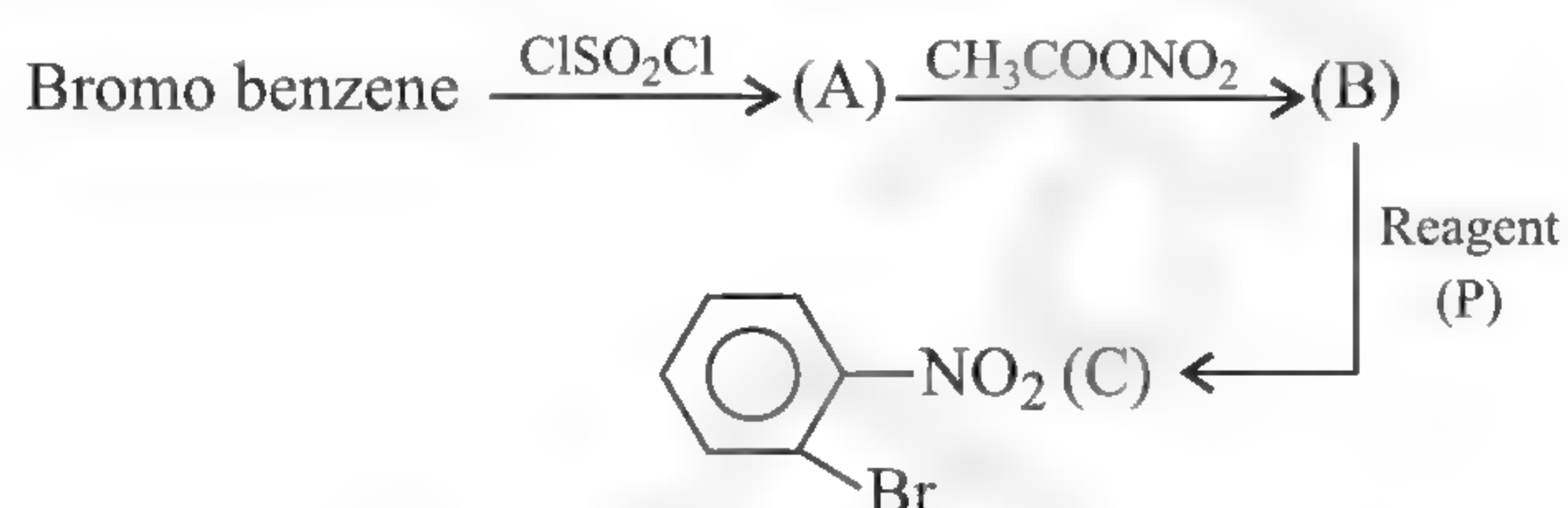
22. Which of the following compound was used as an antipyretic sold under the name antifebrin?

- (1) Benzaldehyde
- (2) Acetanilide
- (3) Paracetamol
- (4) 2-Acetyl salicylic acid

23. Which of the following reactions represents Schotten-Baumann reaction?

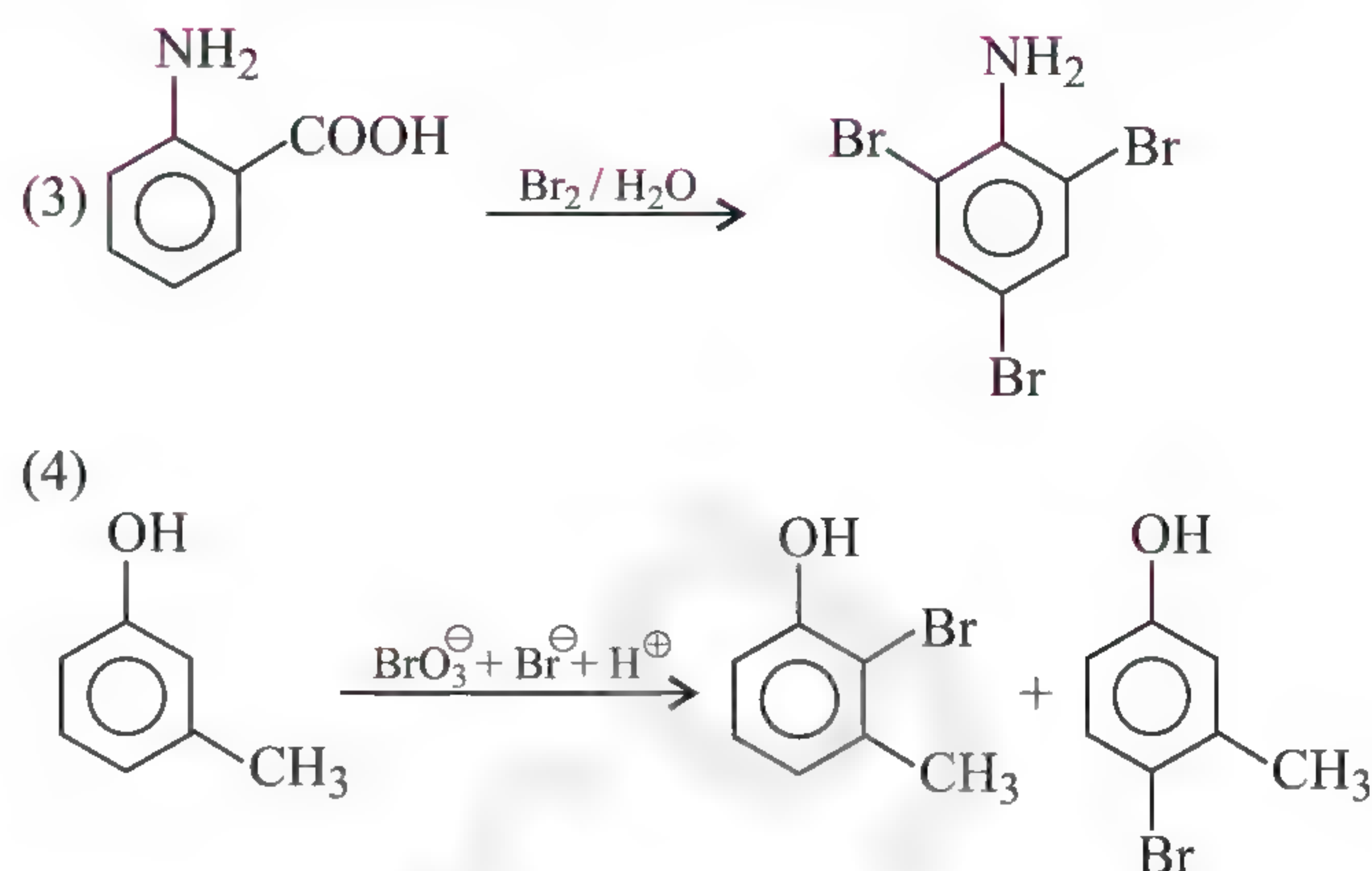
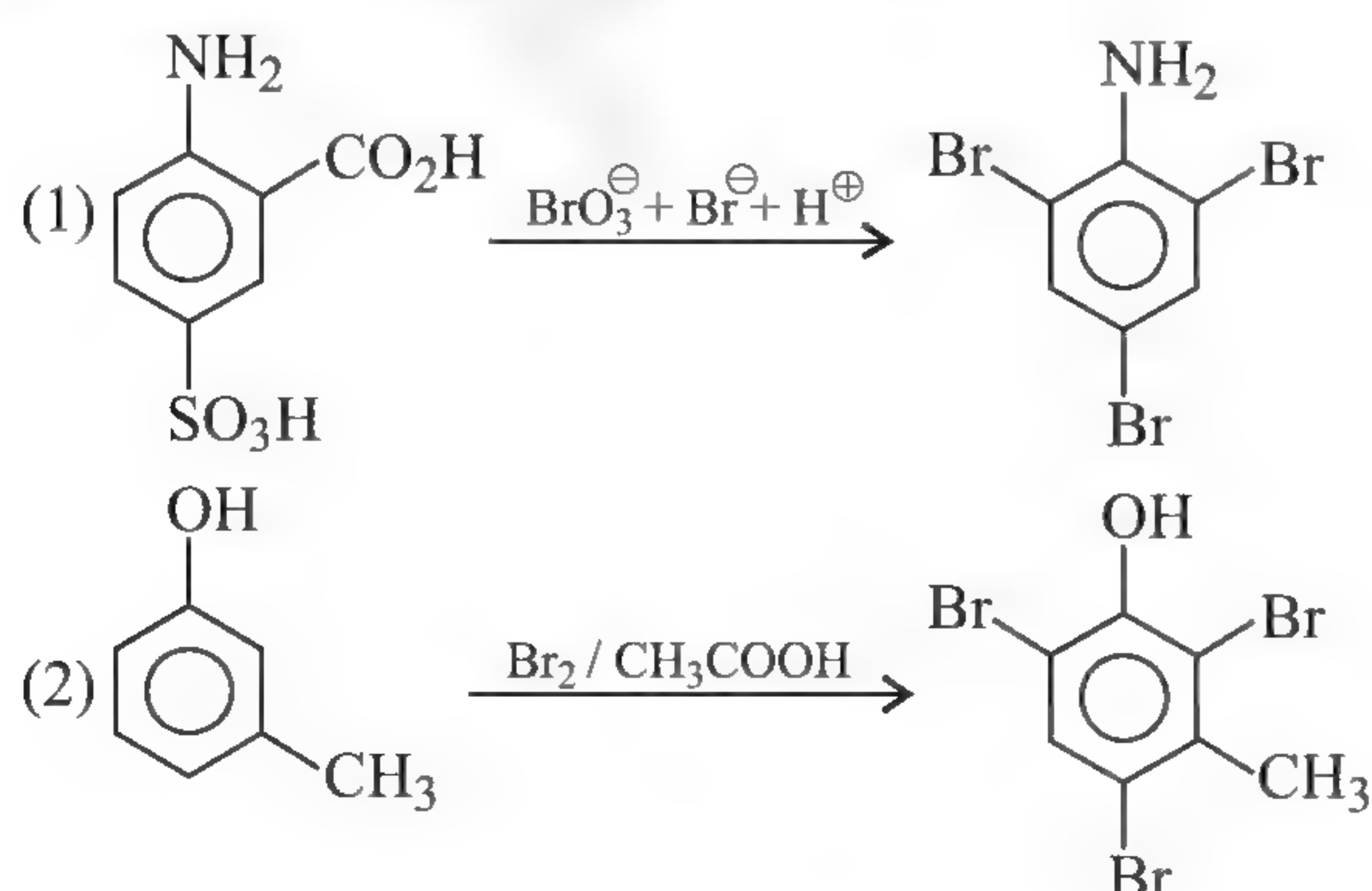
- (1) Aniline $\xrightarrow[+CH_3COOH]{(CH_3CO)_2O}$
- (2) Aniline $\xrightarrow[+NaOH]{PhCOCl}$
- (3) Phenol $\xrightarrow[+Pyridine]{CH_3COCl}$
- (4) *o*-Cresol $\xrightarrow[+H_2SO_4]{(CH_3CO)_2O}$

24. In the following reaction sequence, the reagent (P) is:

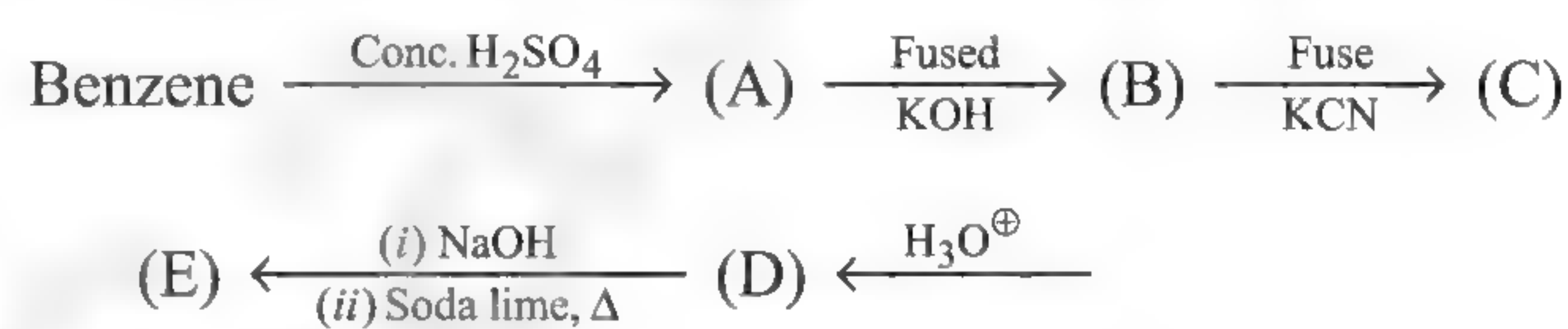


- (1) H_2SO_4 , steam and heat
- (2) HCl/H_2O at 150°
- (3) $NO_2^+ClO_4^-$
- (4) Both (1) and (2)

25. Which of the following is incorrect?



26. In the following reaction sequence, product (E) is:

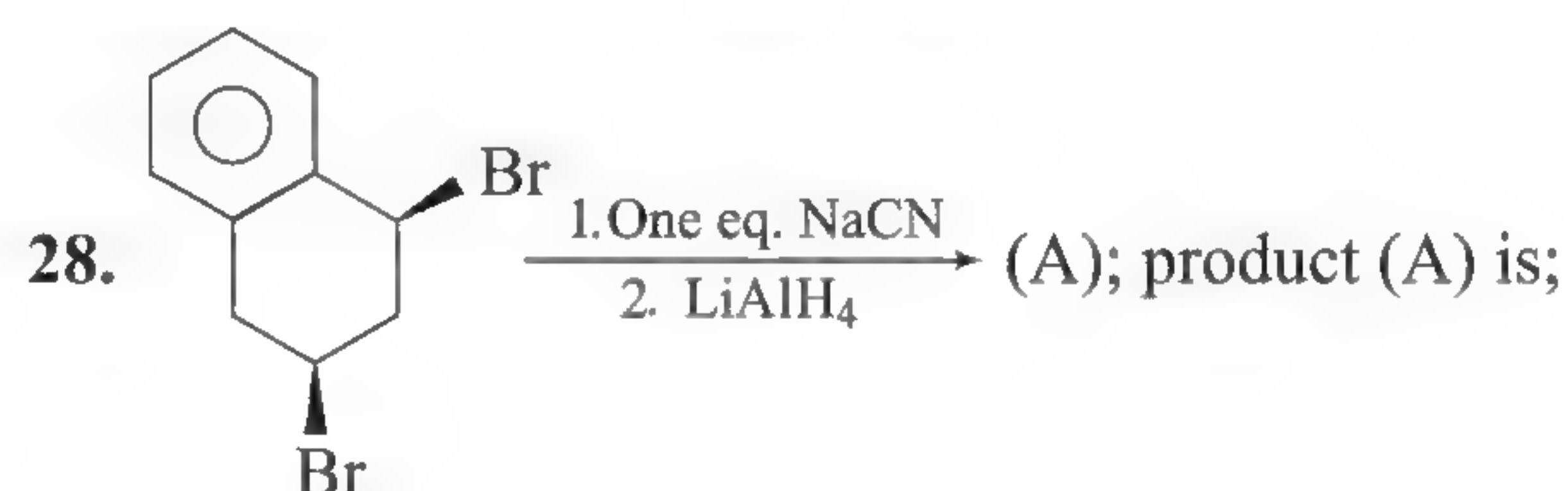


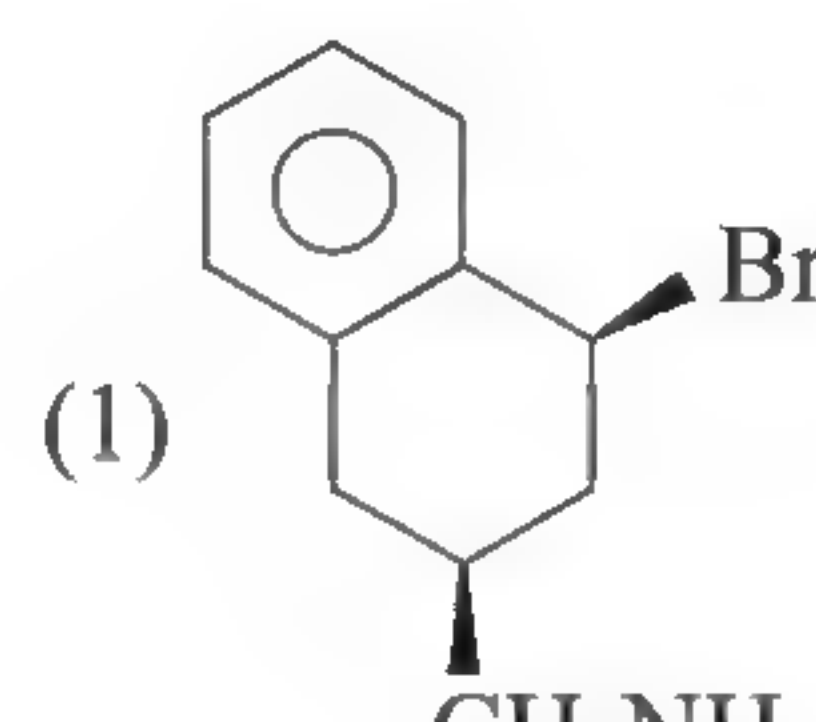
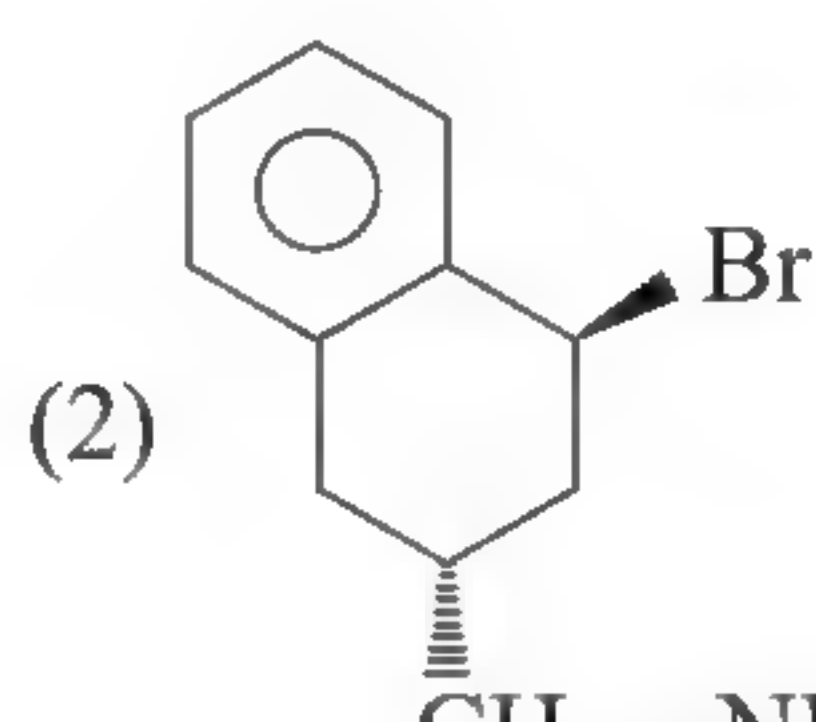
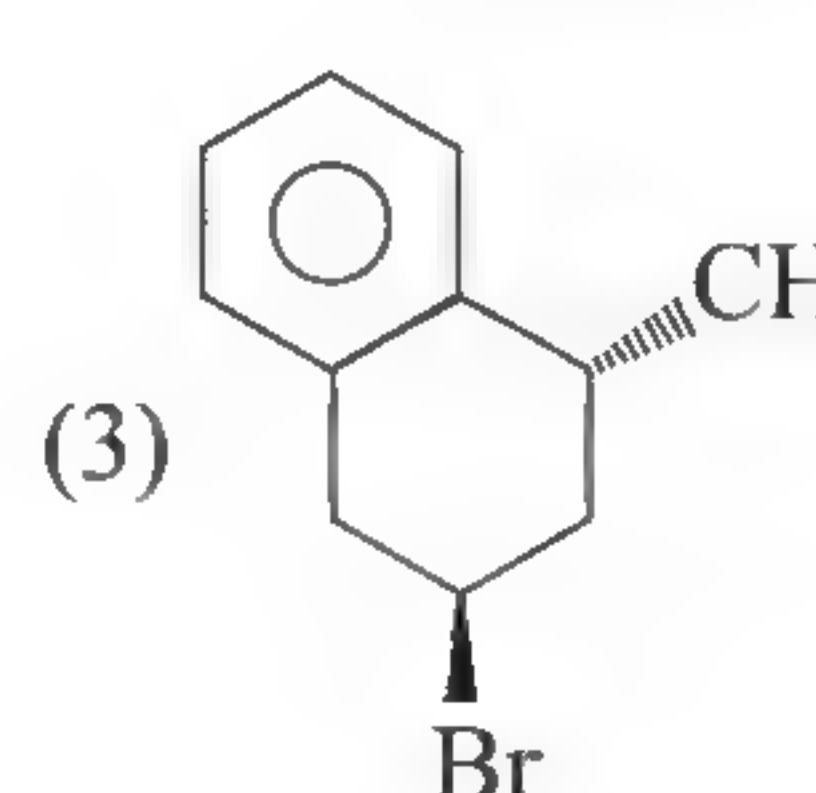
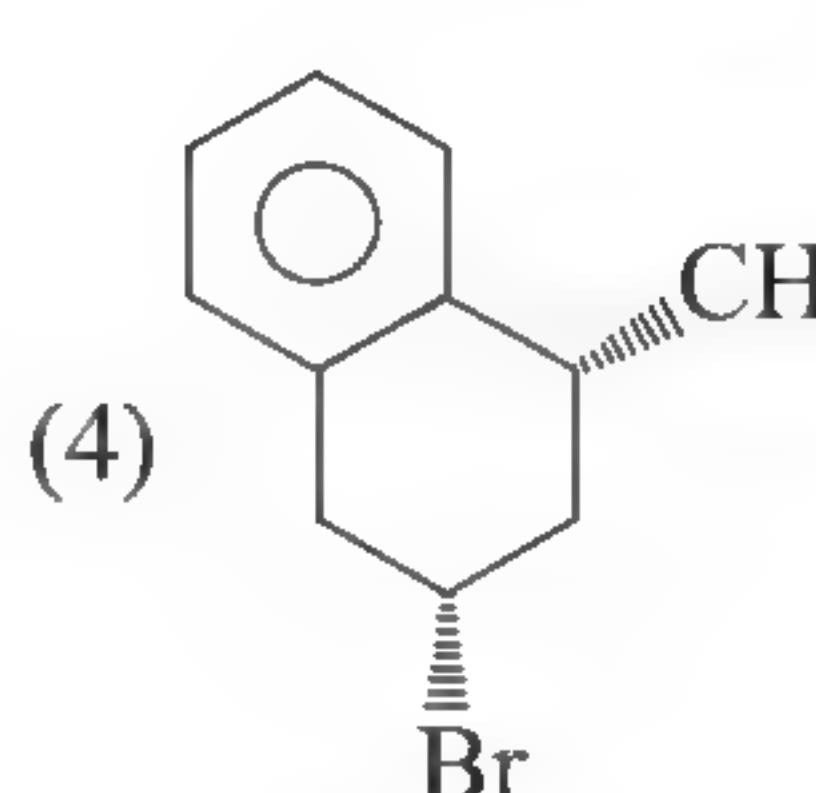
- (1) Benzoic acid
- (2) Phenyl cyanide
- (3) Benzyl amine
- (4) Benzene

27. Which of the following reaction sequences gives picric acid in 100% yield?

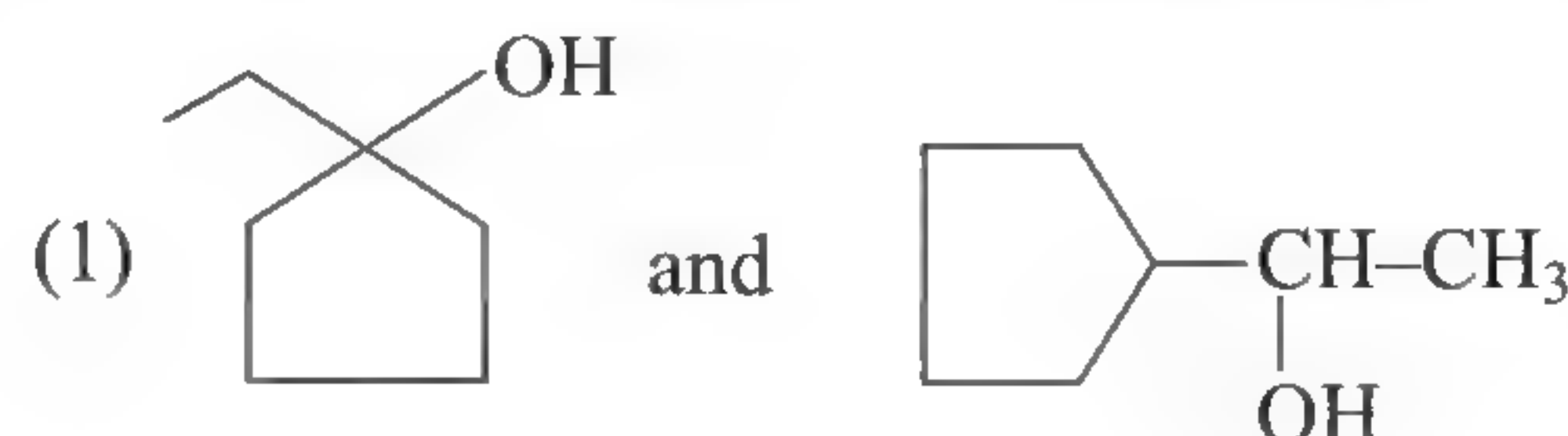
- (1) Phenol $\xrightarrow{\text{Nitration}}$?
- (2) Phenol $\xrightarrow[280\text{ K}]{HNO_2}$? $\xrightarrow{\text{Dil. } HNO_3}$?
- (3) Phenol $\xrightarrow[373\text{ K}]{\text{Conc. } H_2SO_4}$? $\xrightarrow[\Delta]{\text{Conc. } HNO_3}$?
- (4) All.

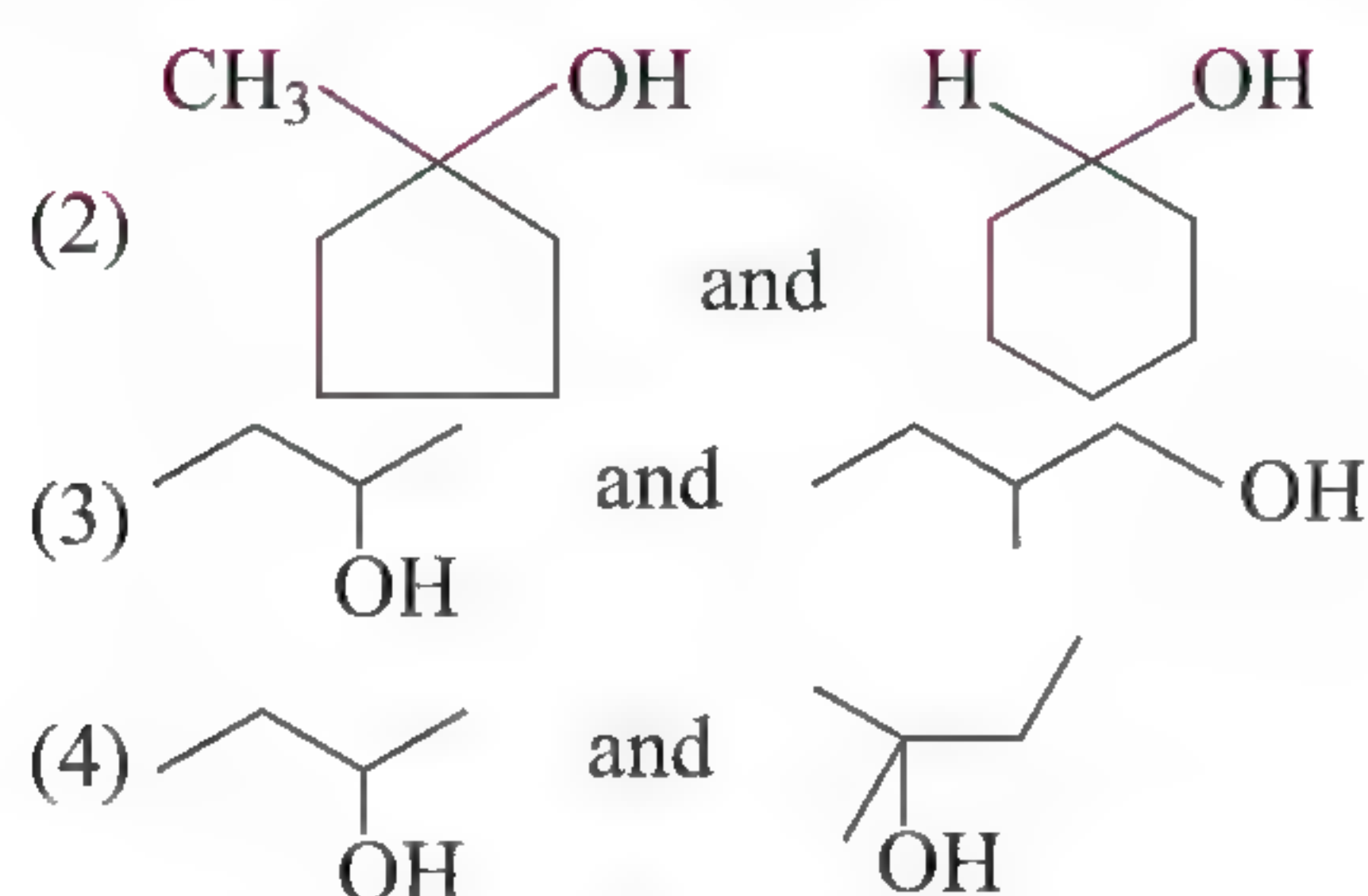
Reactions, Properties of Alkyl and Aryl Halides



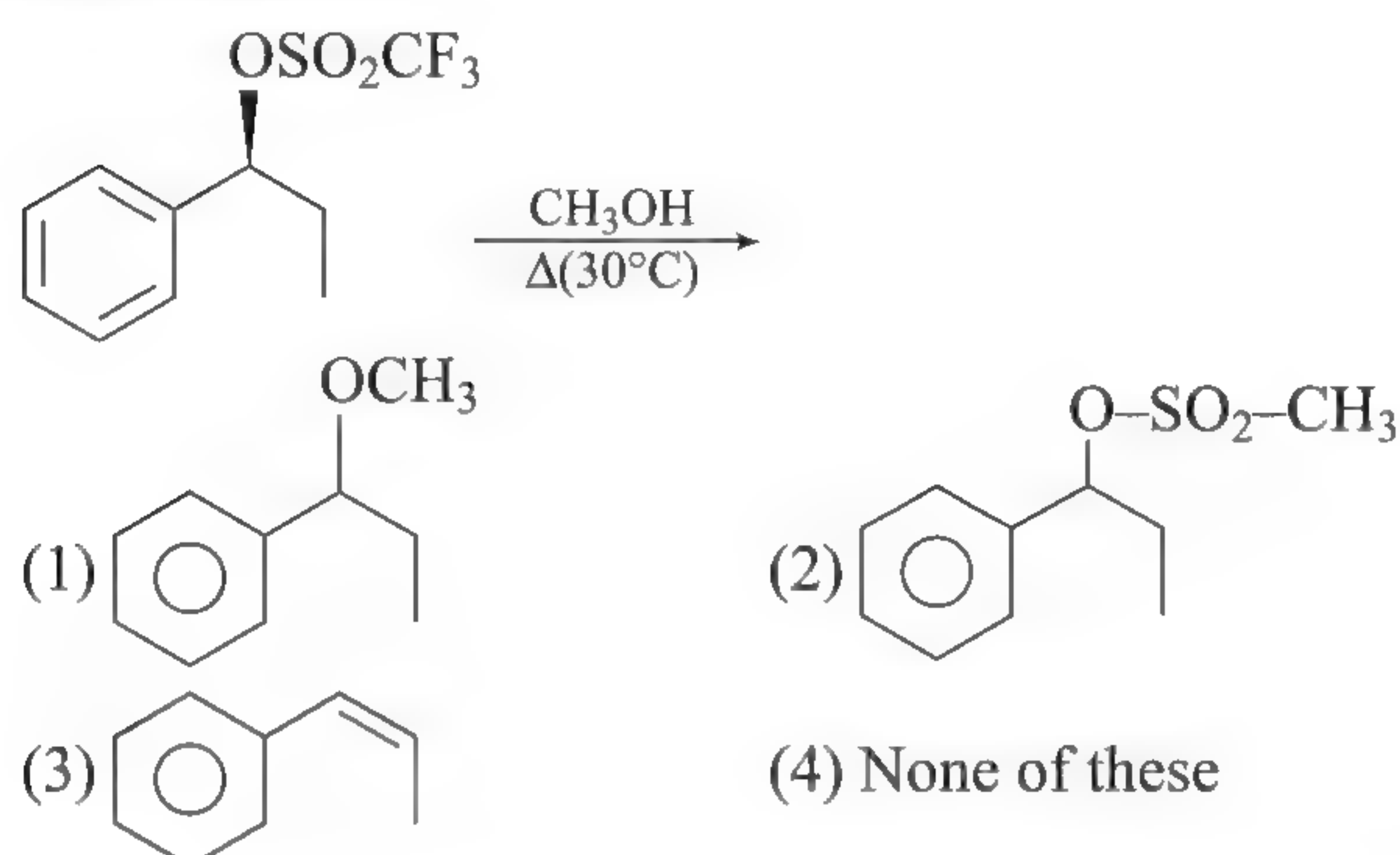
- (1) 
- (2) 
- (3) 
- (4) 

29. In the given pair of alcohols, in which pair second alcohol is more reactive than first towards hydrogen bromide?

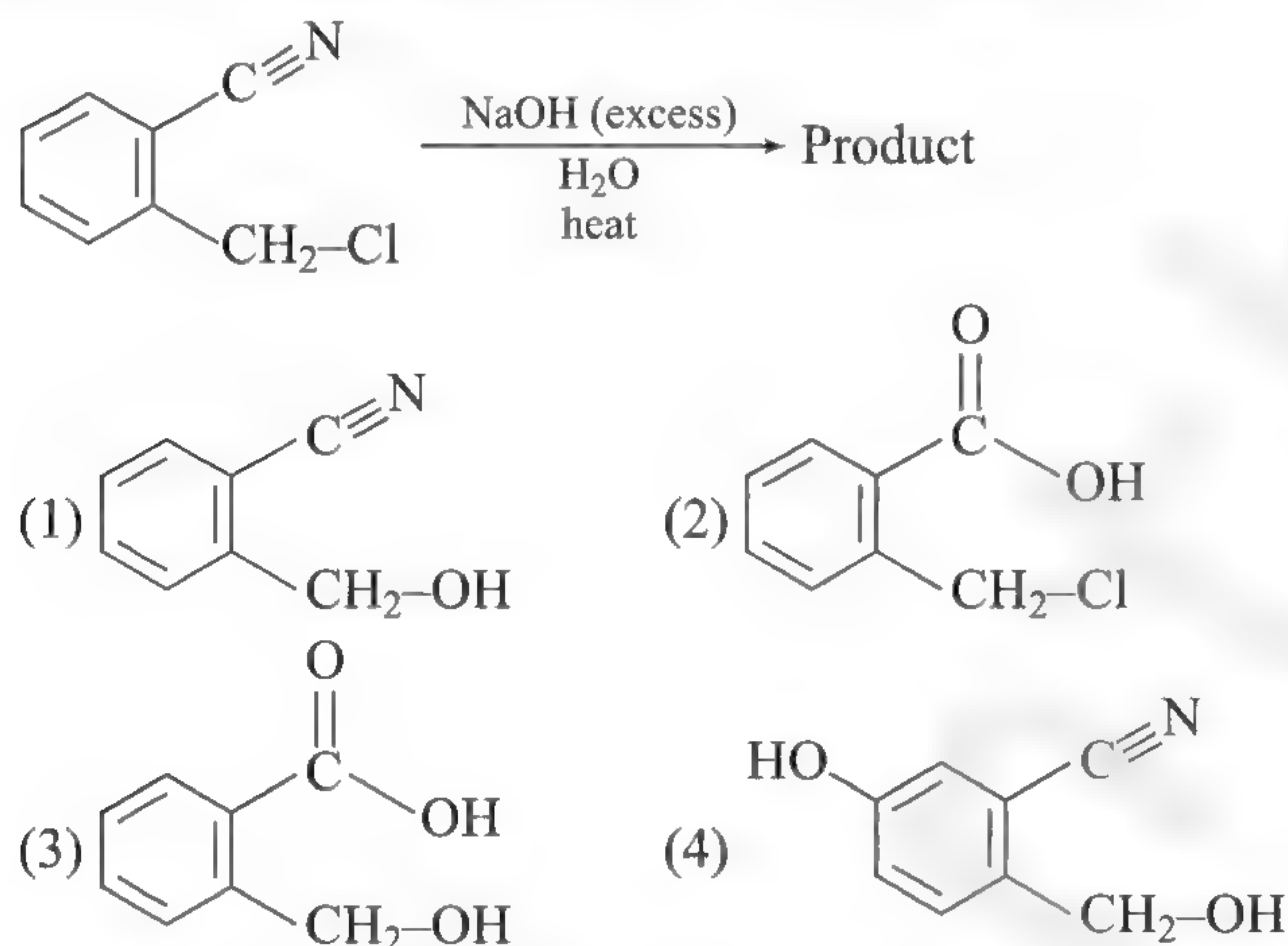




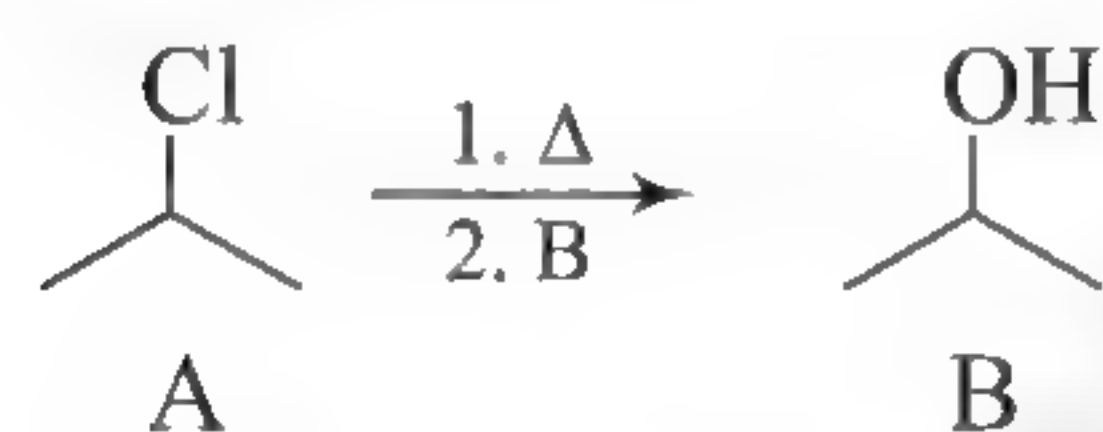
30. Which product would be expected to predominate in the given reaction?



31. Which is the major product of the following reaction?

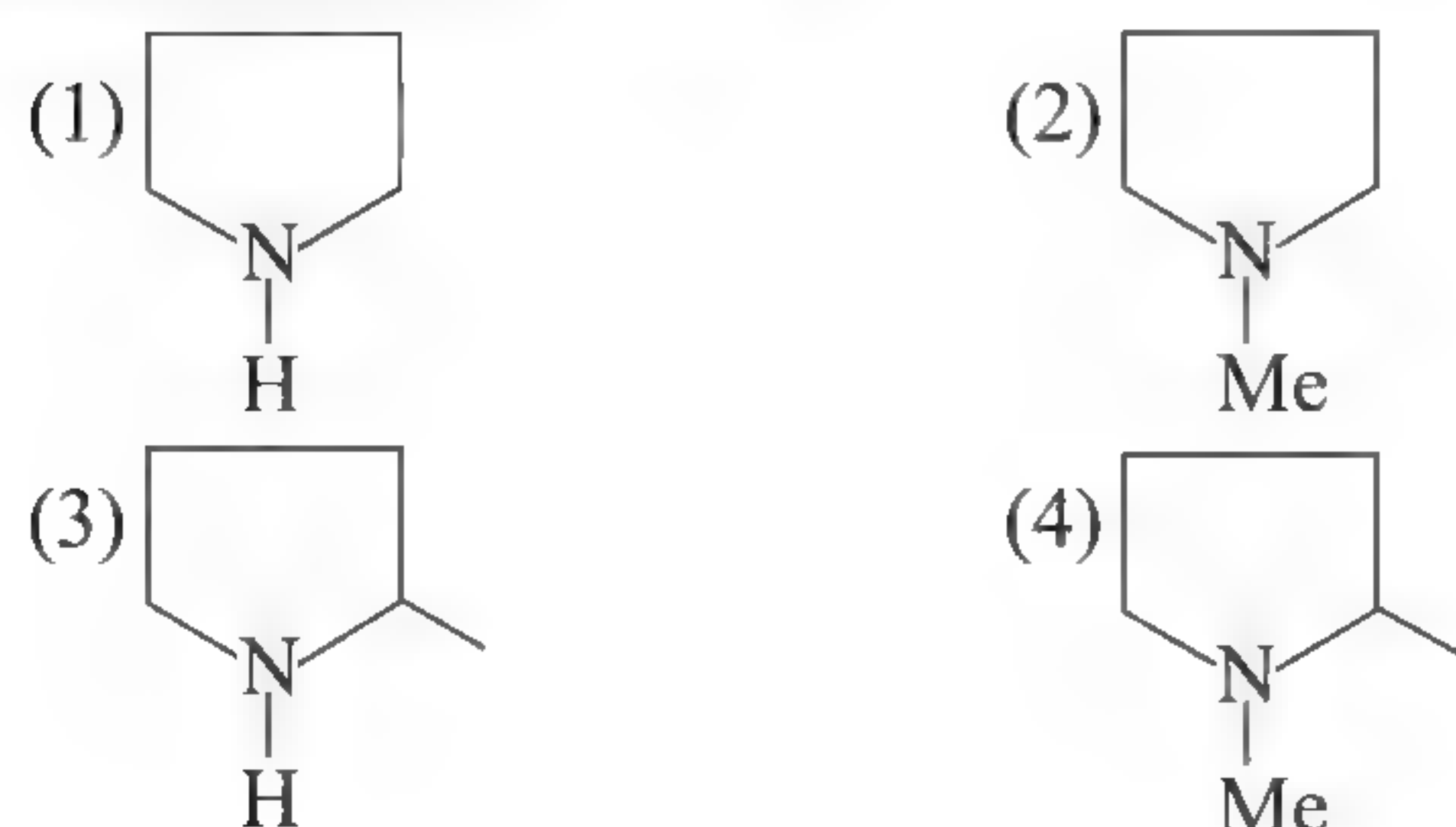


32. Which of the following reagents shown below would accomplish the following transformations?



- | | |
|----------------------------|--|
| (1) NaOH | $\text{BH}_3\text{-THF; H}_2\text{O}_2/\text{NaOH}$ |
| (2) H_3O^+ | $\text{BH}_3\text{-THF; H}_2\text{O}_2/\text{NaOH}$ |
| (3) HBr in ether | $\text{Hg}(\text{OAc})_2/\text{H}_2\text{O; NaBH}_4$ |
| (4) NaNH_2 | $\text{Hg}(\text{OAc})_2/\text{H}_2\text{O; NaBH}_4$ |

33. $\text{Cl-CH}_2\text{-(CH}_2\text{)}_2\text{-CH}_2\text{-Cl} + \text{CH}_3\text{NH}_2 \rightarrow$ Product of the reaction is:

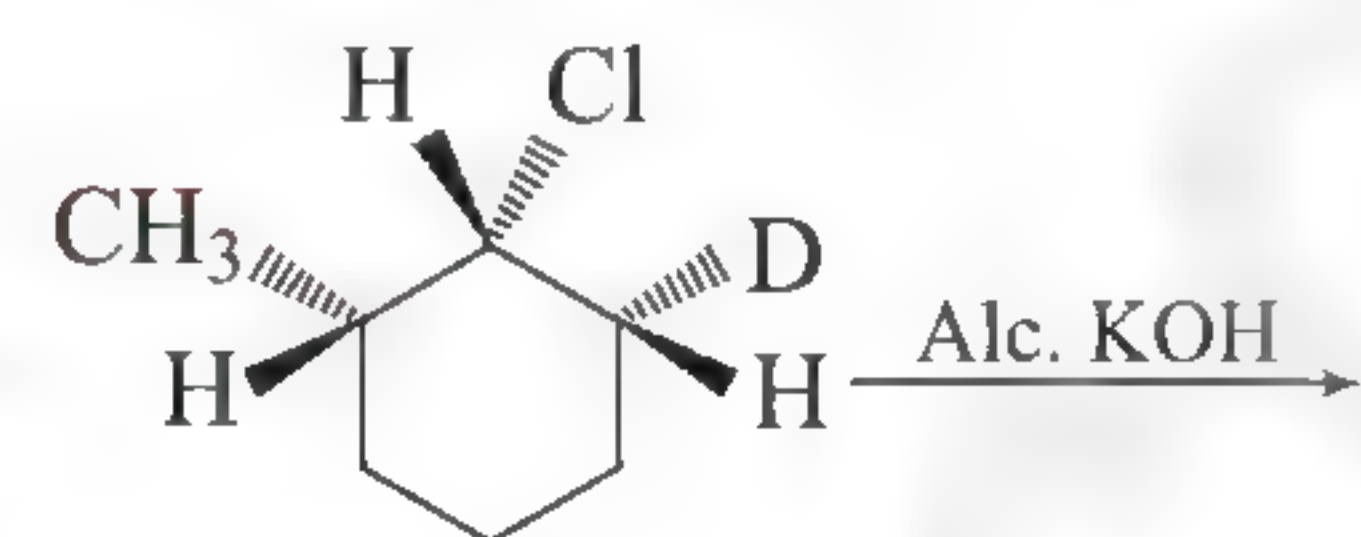


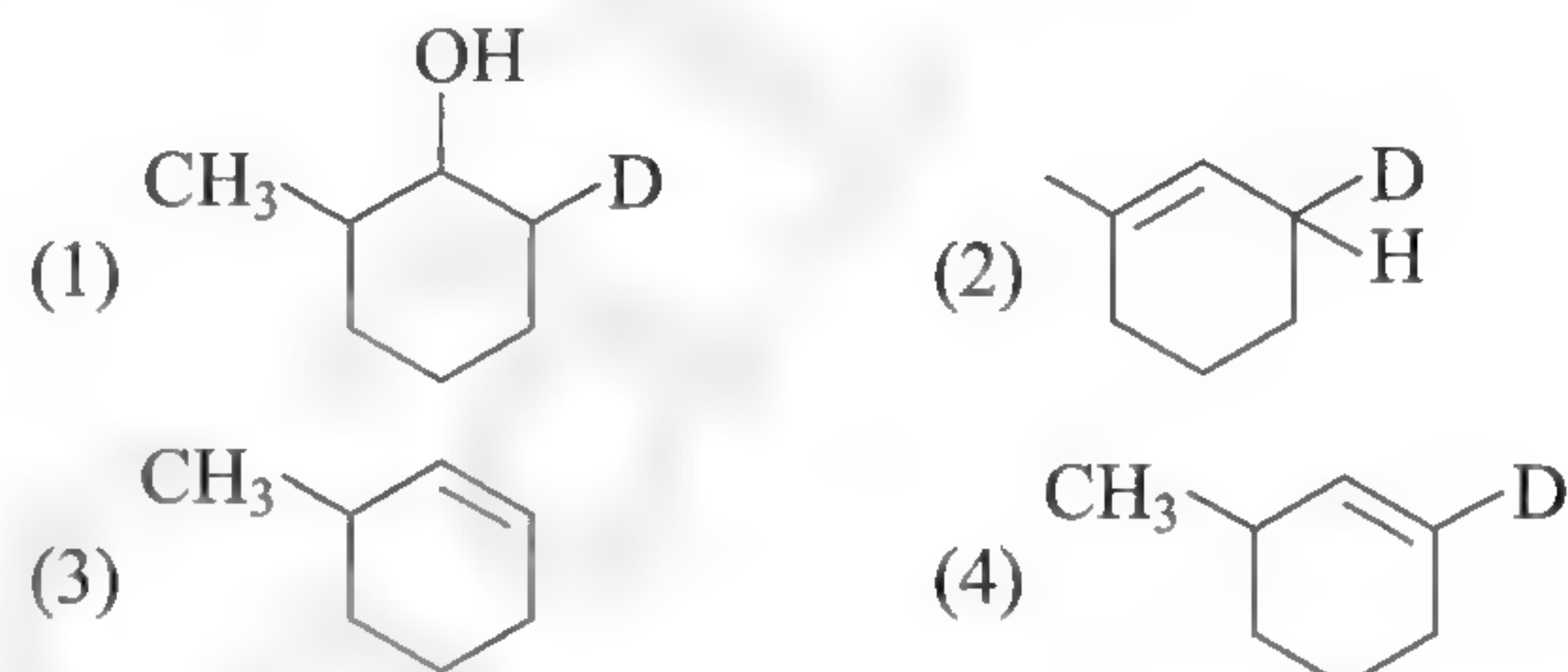
34. Which alkyl halide has maximum density?

- (1) $\text{C}_3\text{H}_7\text{I}$ (2) CH_3Br
 (3) CH_3I (4) $\text{C}_2\text{H}_5\text{I}$

35. Which of the following molecules would have a carbon-halogen bond most susceptible to nucleophilic substitution?

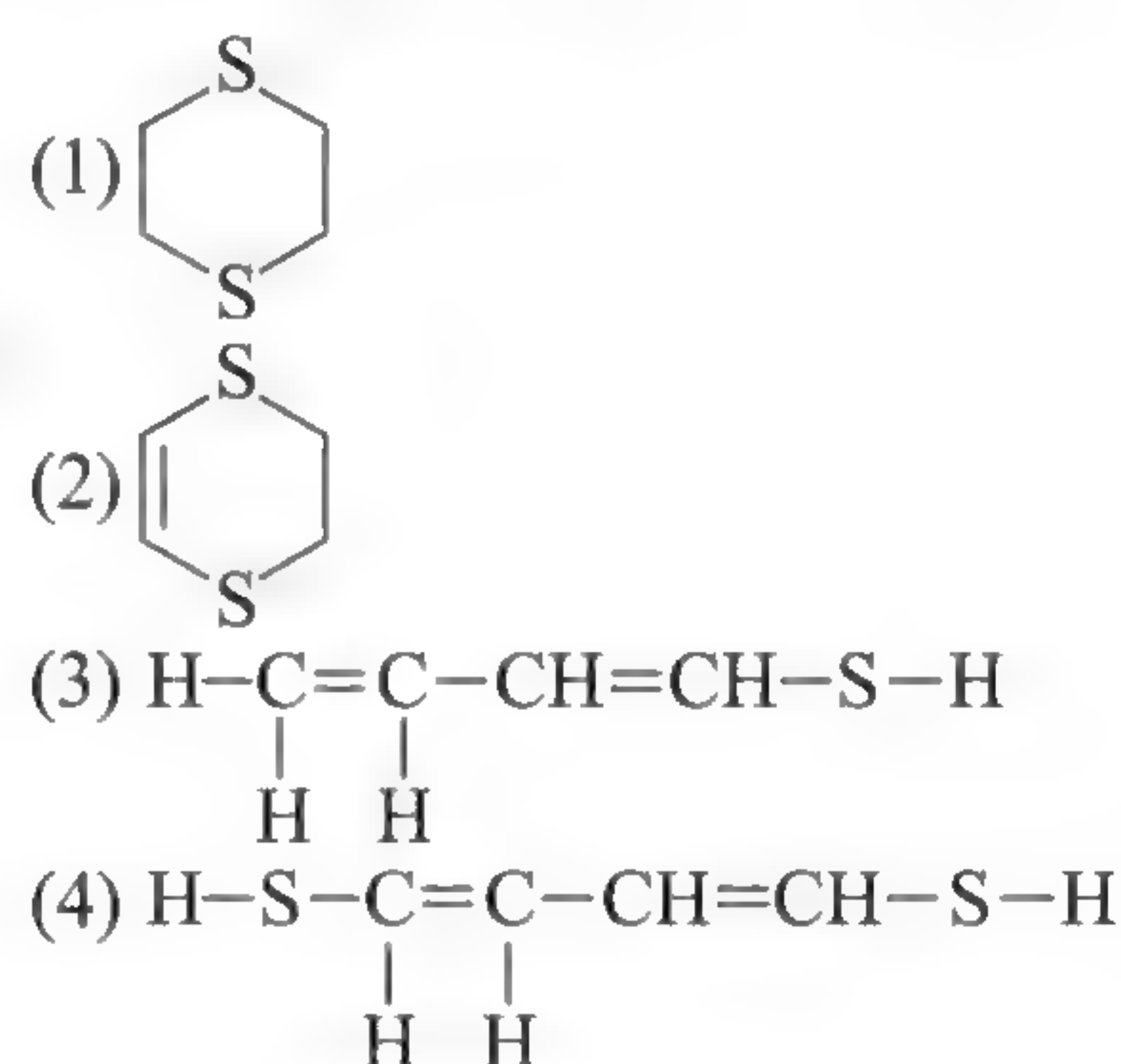
- (1) 2-chlorobutane (2) 2-fluorobutane
 (3) 2-bromobutane (4) 2-iodobutane

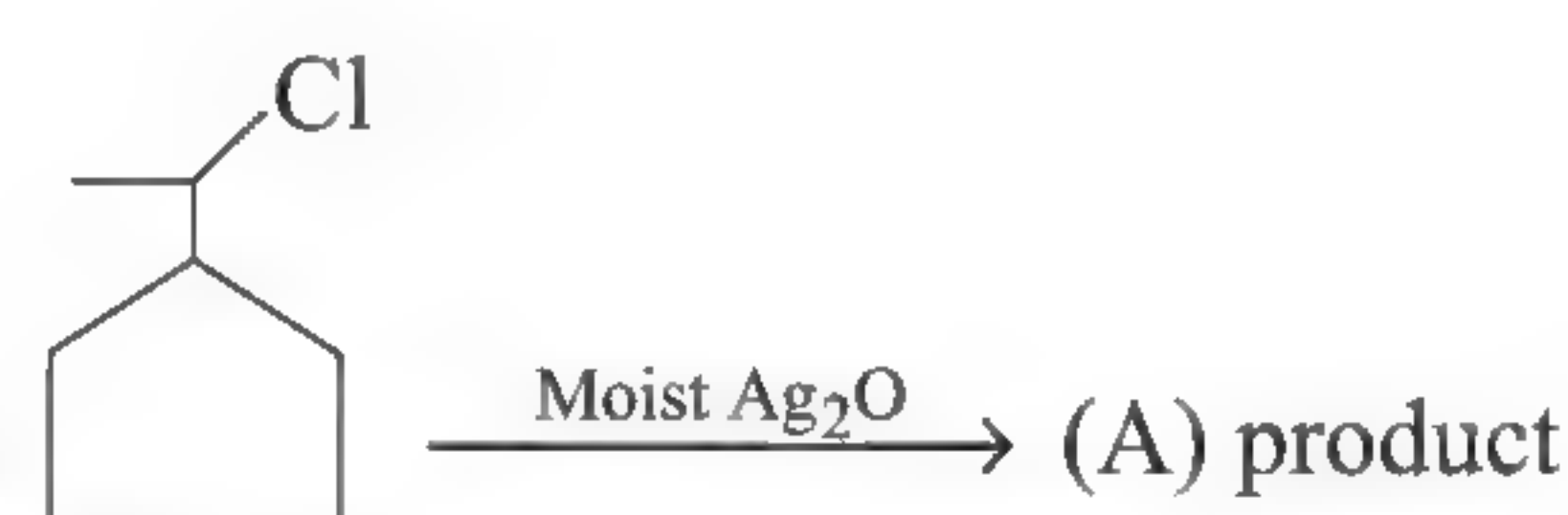
36.  (A); Major product of this reaction is:

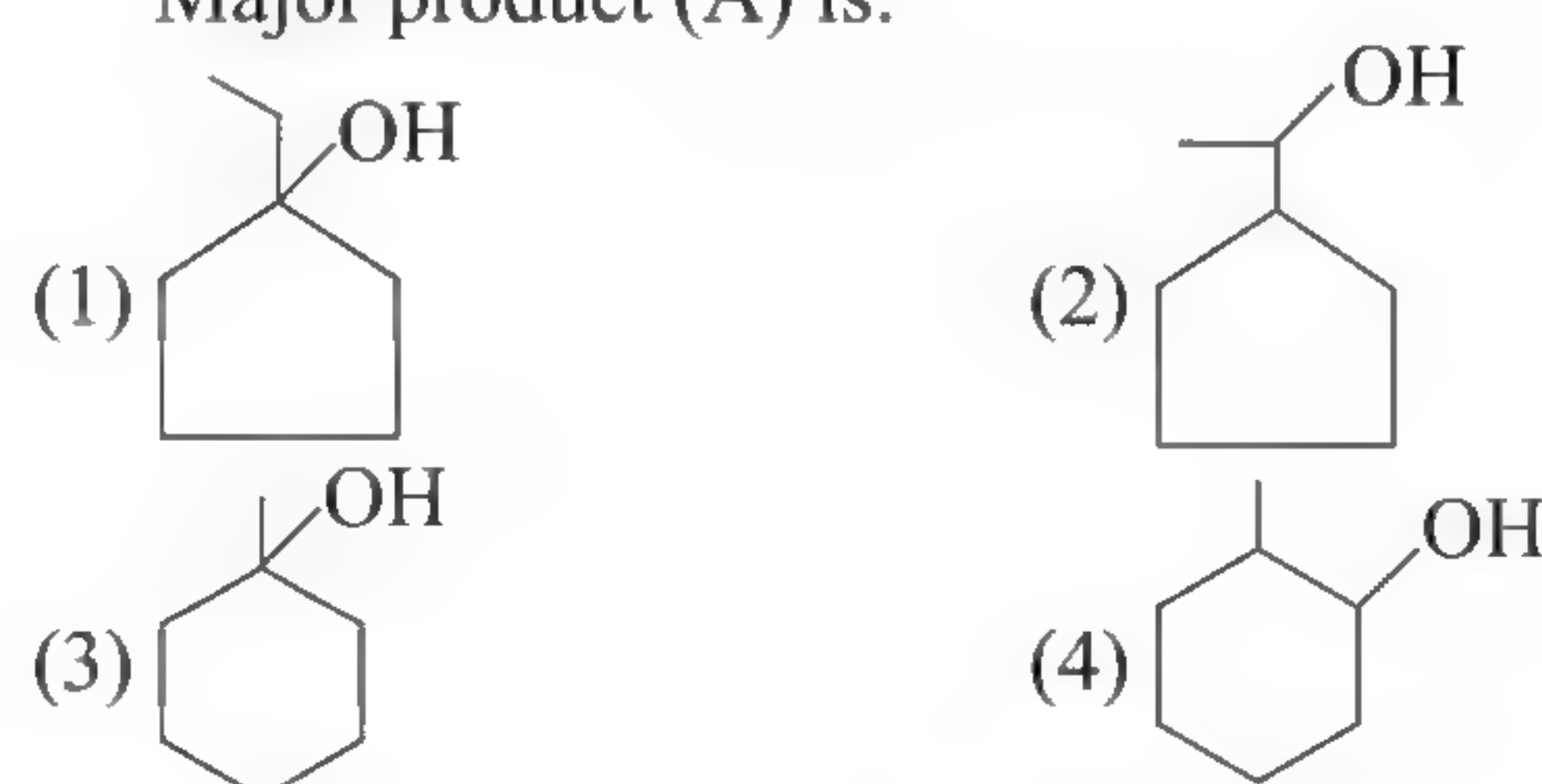


37. $1\text{-}2\text{-dibromo ethane} + \text{NaSCH}_2\text{CH}_2\text{SNa} \rightarrow \text{C}_4\text{H}_8\text{S}_2$; (B)

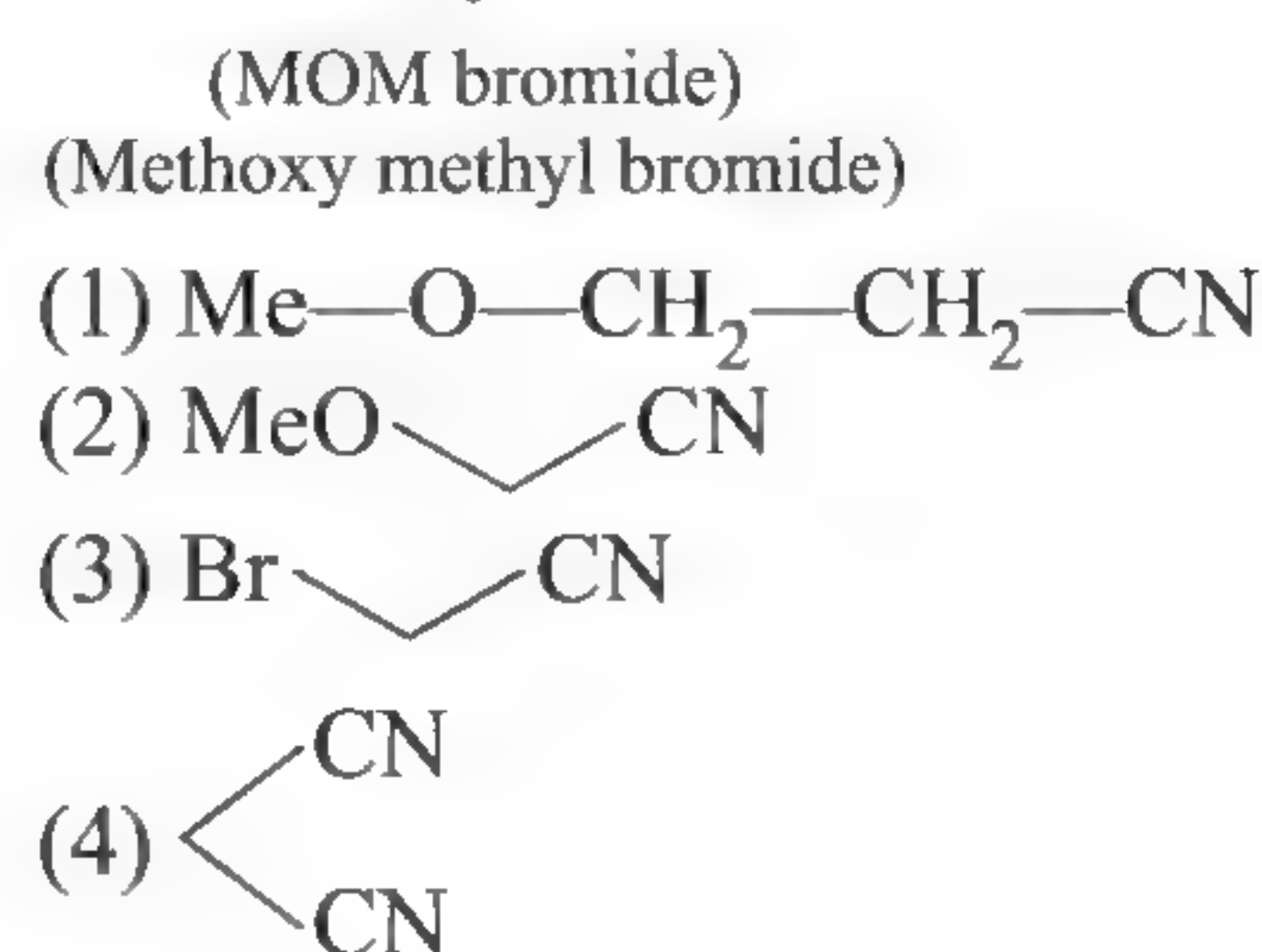
Unknown product (B) of the above reaction is:



38.  (A) product
 Major product (A) is:



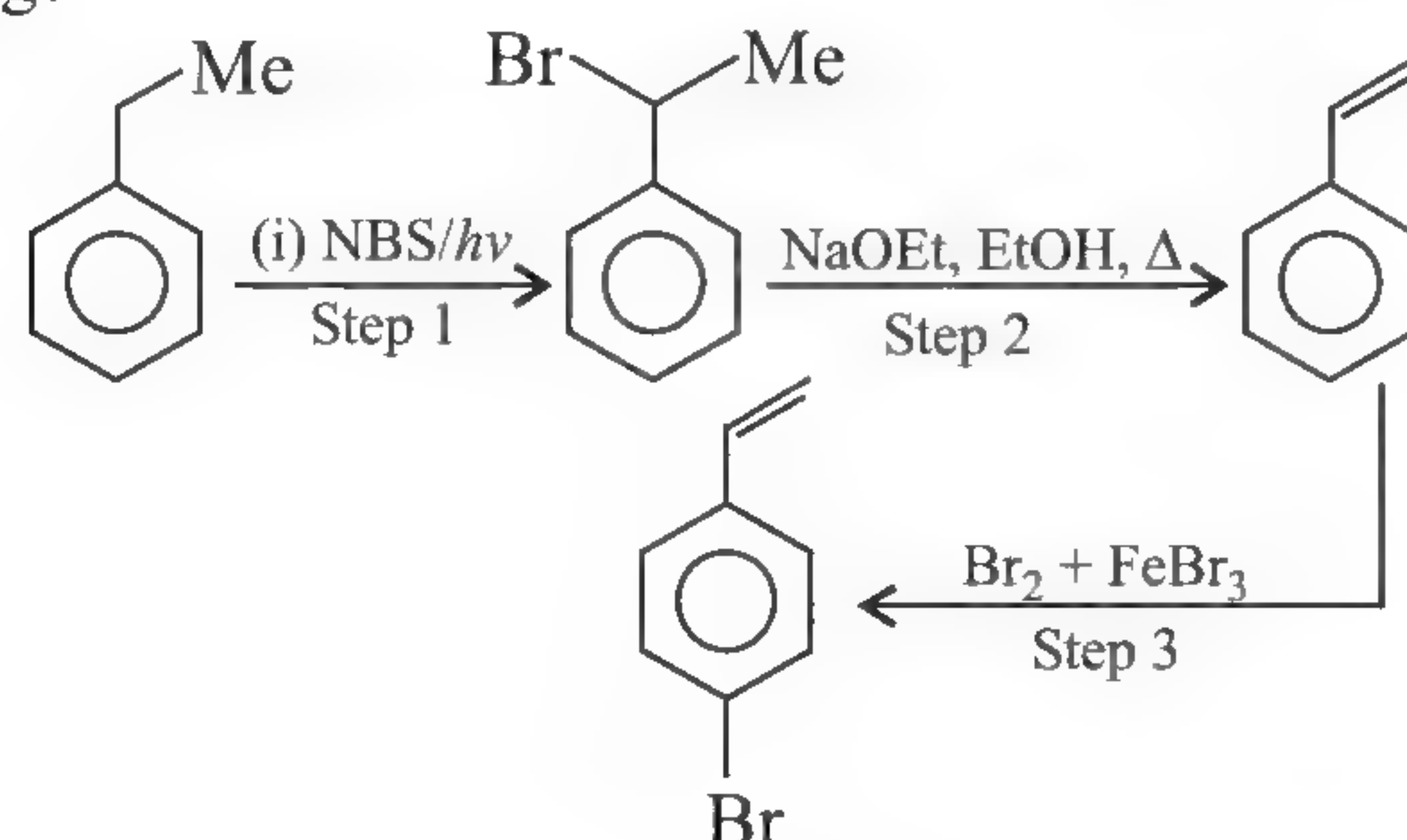
39. $\text{MeO-CH}_2\text{-Br} \xrightarrow{\text{KCN}}$ Product of reaction is:



40. Which of the following is the most reactive towards nucleophilic substitution reaction?

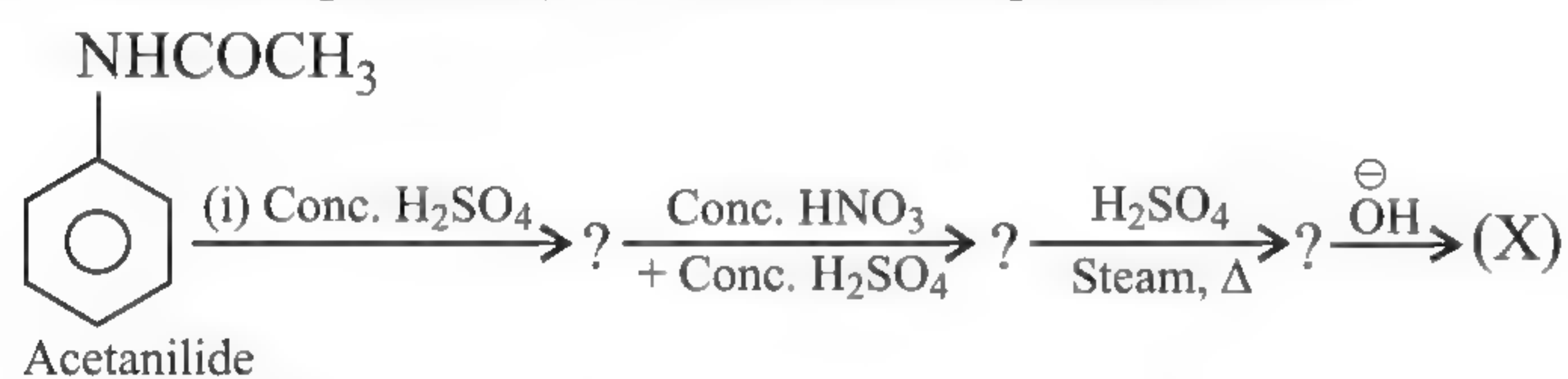
- (1) $\text{C}_6\text{H}_5\text{Br}$ (2) $\text{CH}_2=\text{CH}-\text{Br}$
 (3) $\text{CH}_3\text{CH}=\text{CHBr}$ (4) $\text{BrCH}_2-\text{CH}=\text{CH}_2$

41. In the following reaction, which of the following steps is wrong?



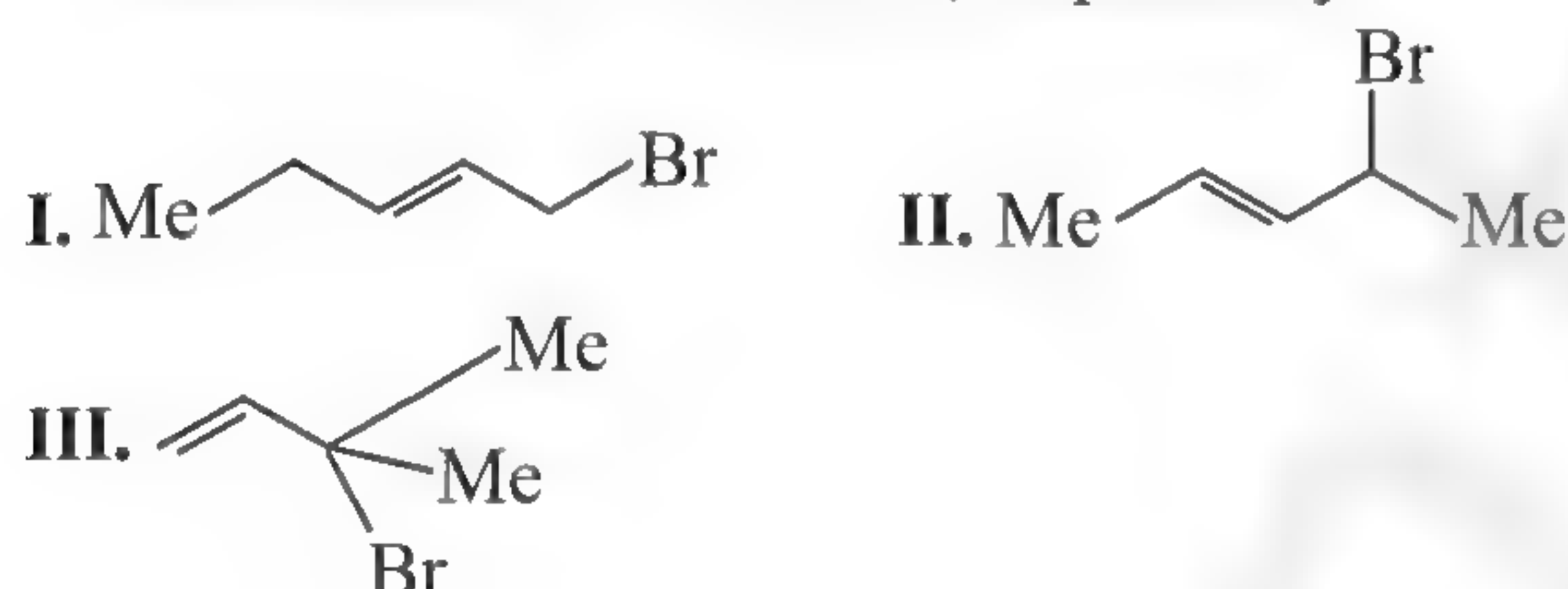
- (1) Step 1 (2) Step 2
 (3) Step 3 (4) None

42. The final product (X) in the following reaction is:



- (1) 2-Nitroaniline (2) 3-Nitroaniline
 (3) 4-Nitroaniline (4) Sulphanilic acid

43. Which of the following halides will be the most reactive in S_N^2 reaction and S_N^1 reaction, respectively?

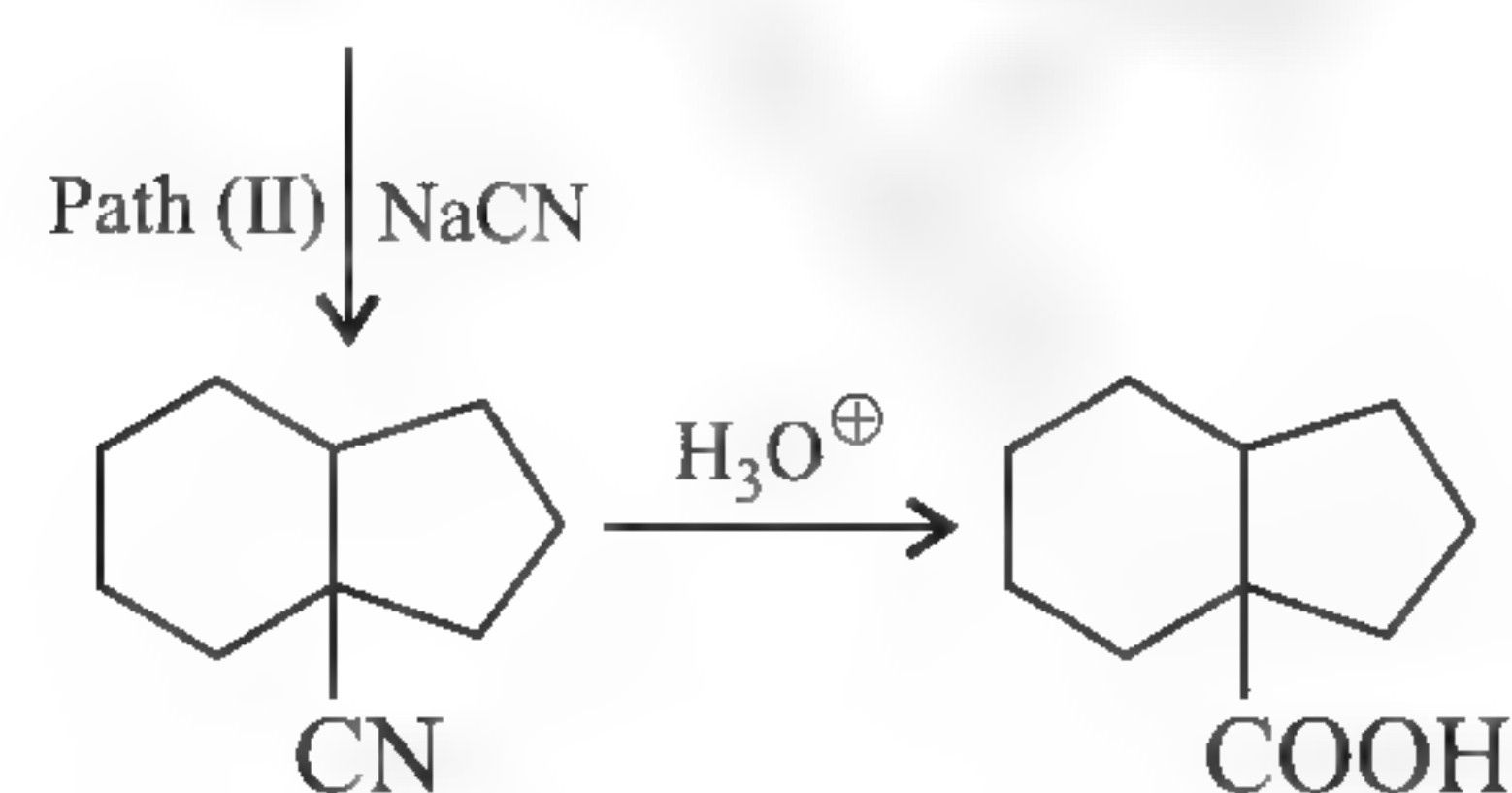
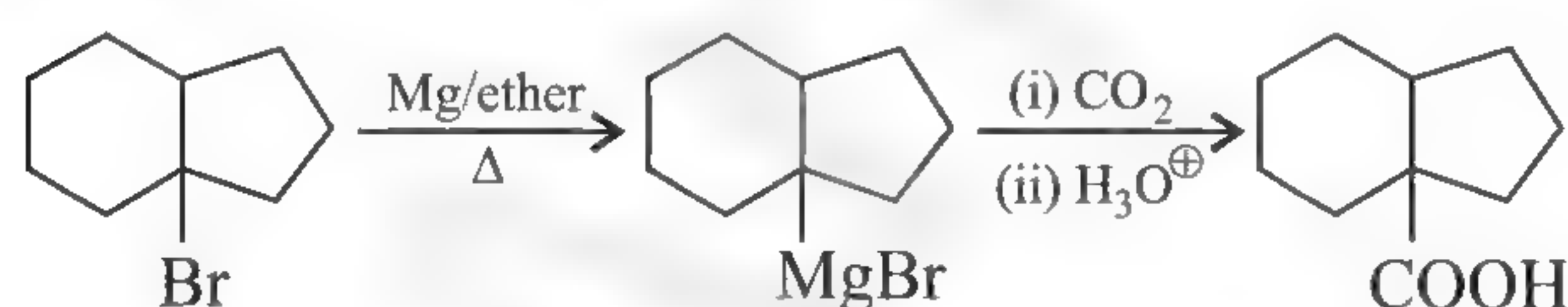


- (1) (I), (II) (2) (II), (I)
 (3) (I), (III) (4) (III), (I)

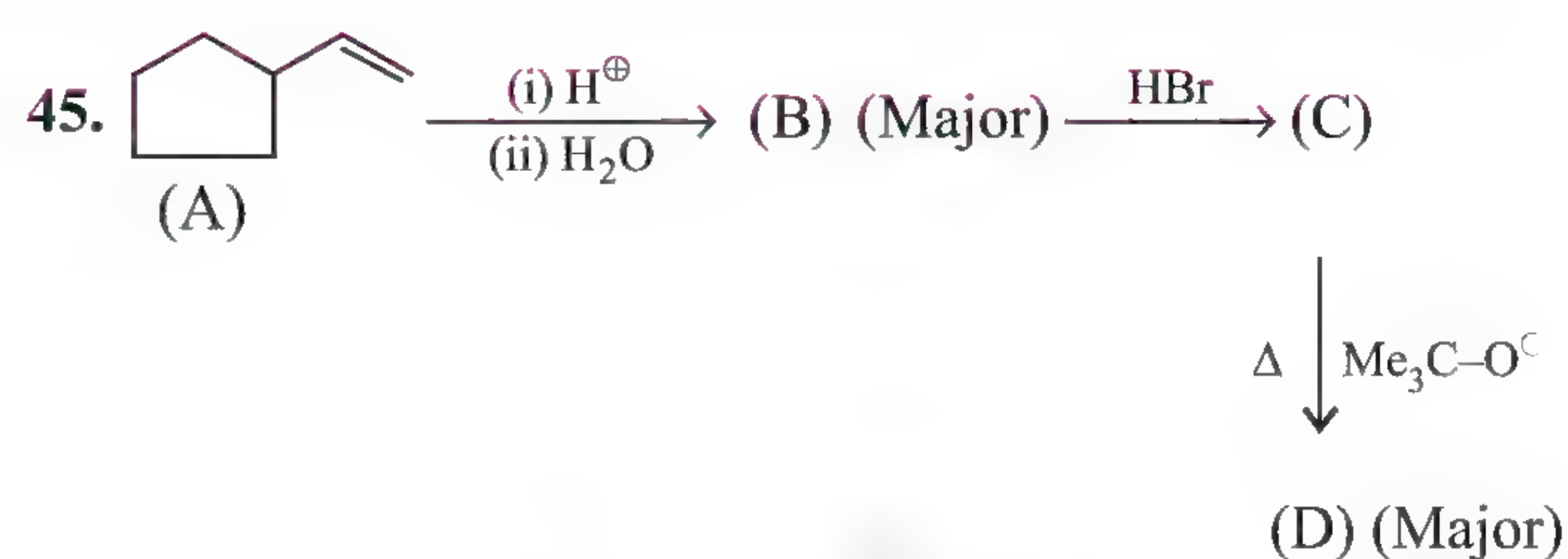
44. In the following reaction, the final product can be prepared by two paths (I) and (II).

Which of the following statements is correct?

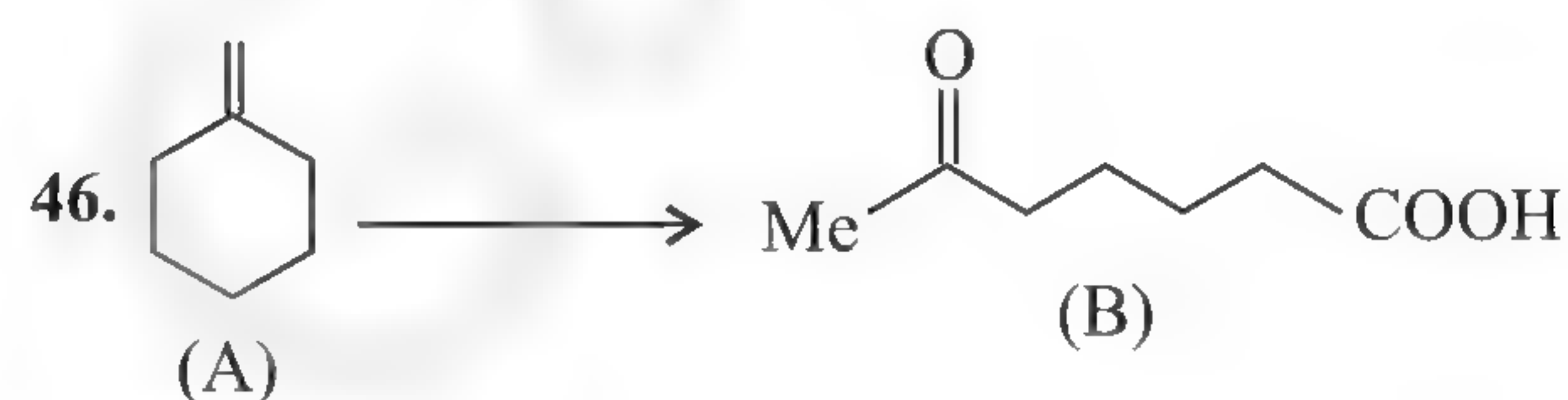
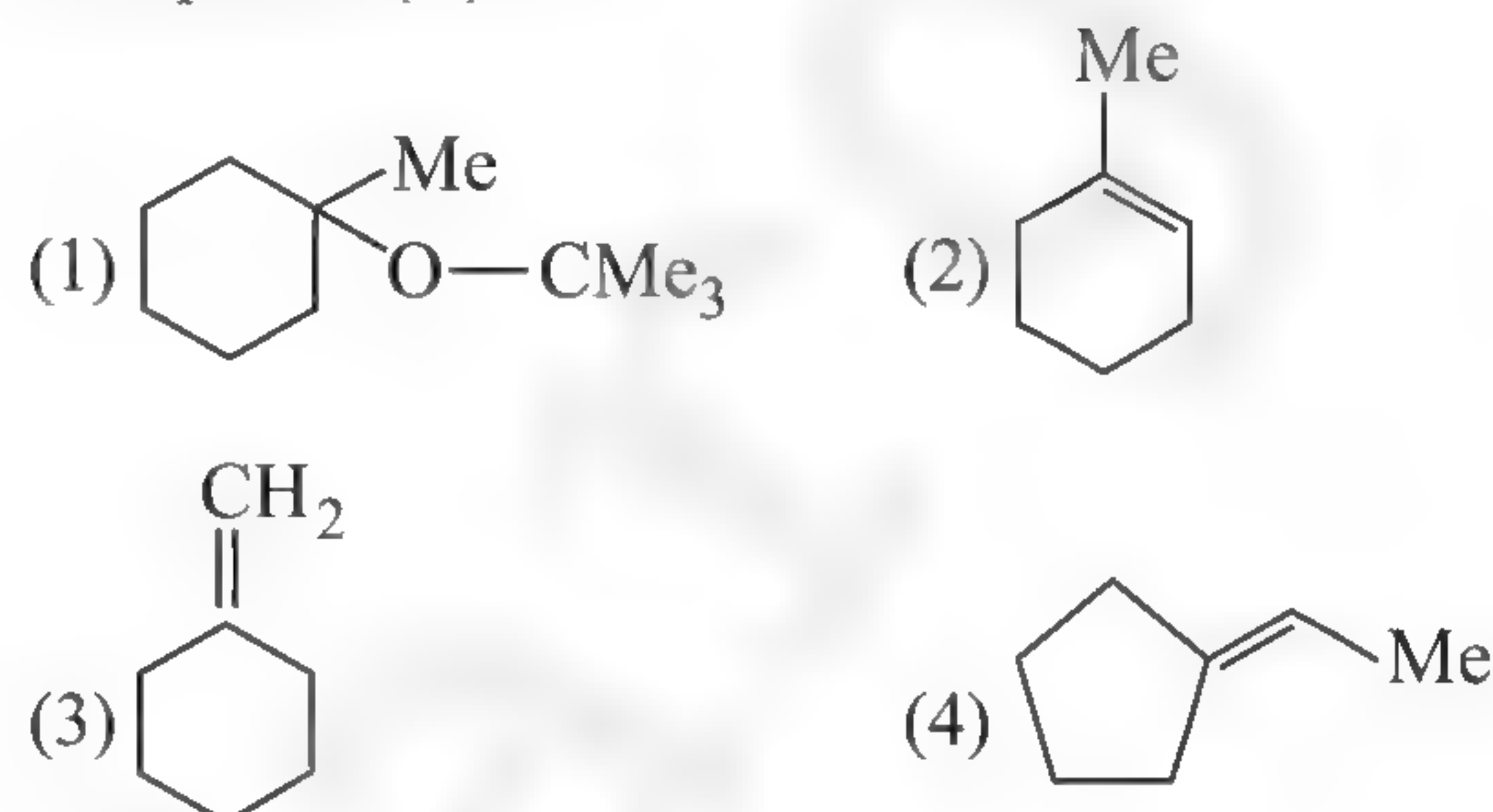
Path (I)



- (1) Path (I) is feasible.
 (2) Path (II) is feasible.
 (3) Both paths are feasible.
 (4) Neither of the two paths is feasible

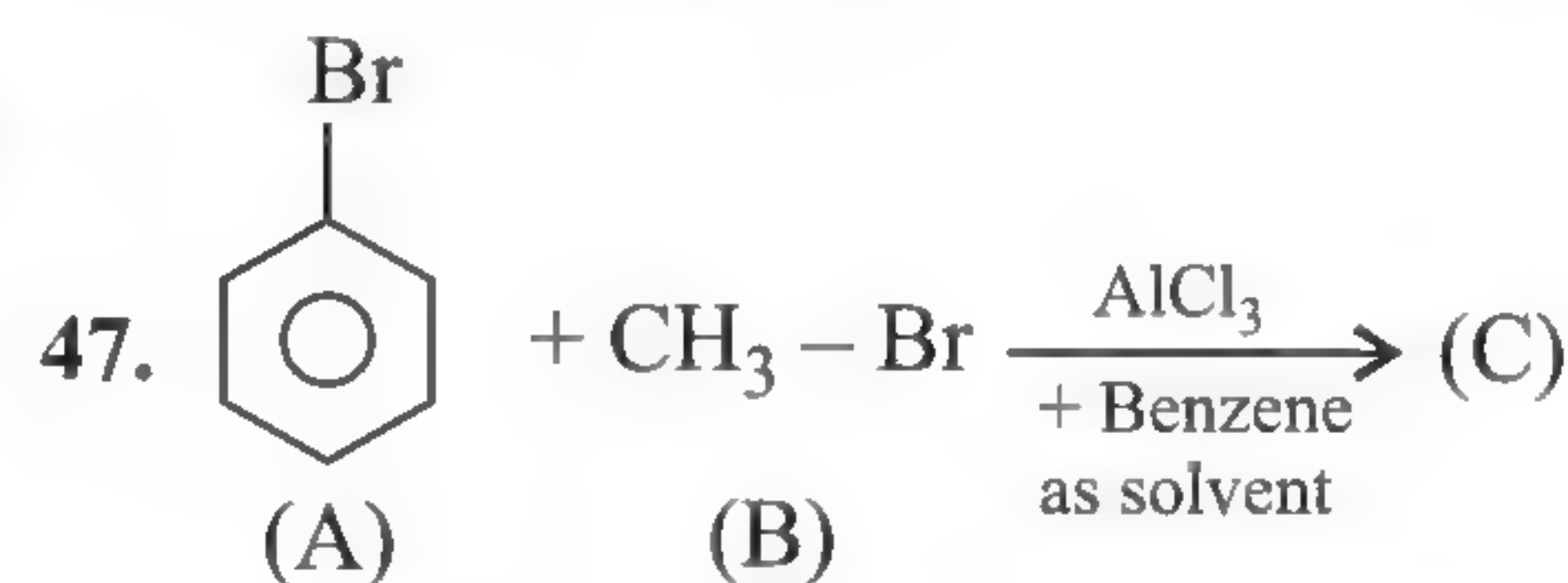


Compound (D) is:

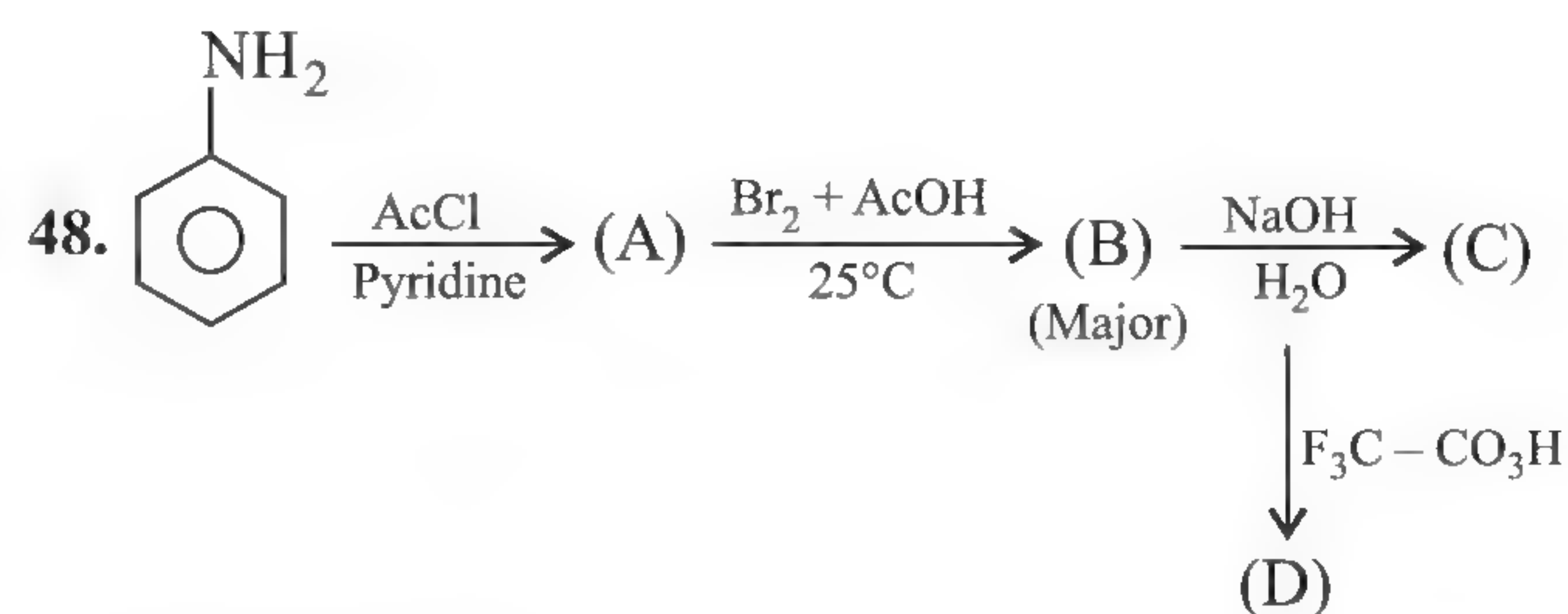
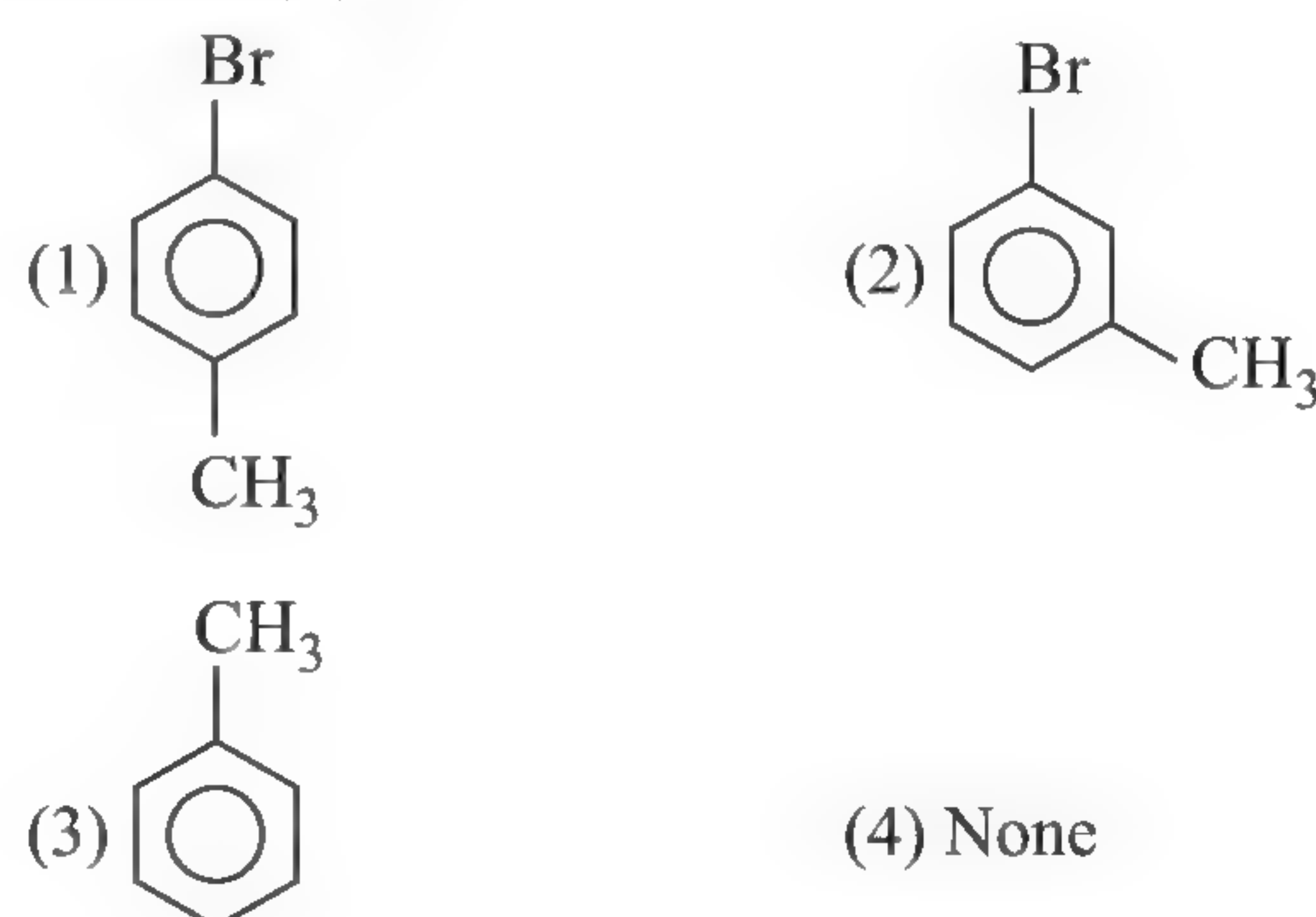


The above conversion can be carried out by which process.

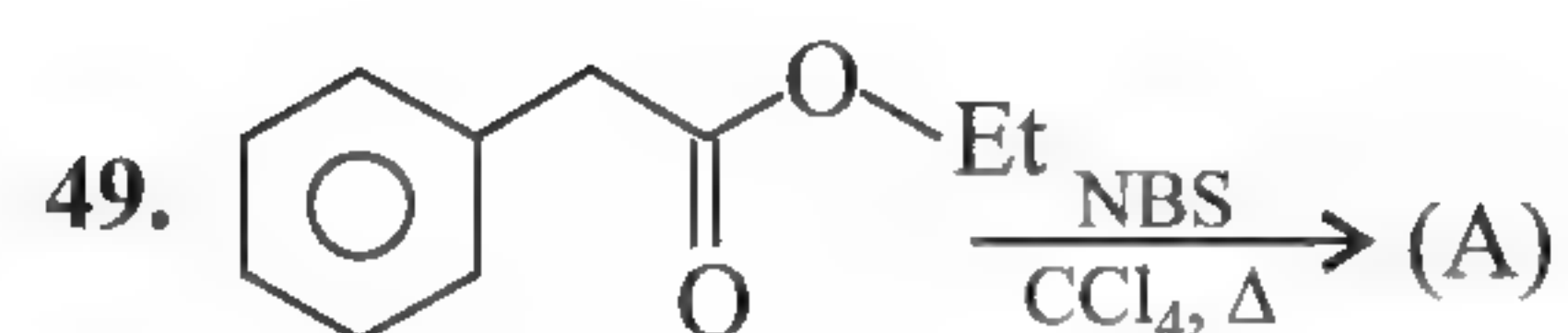
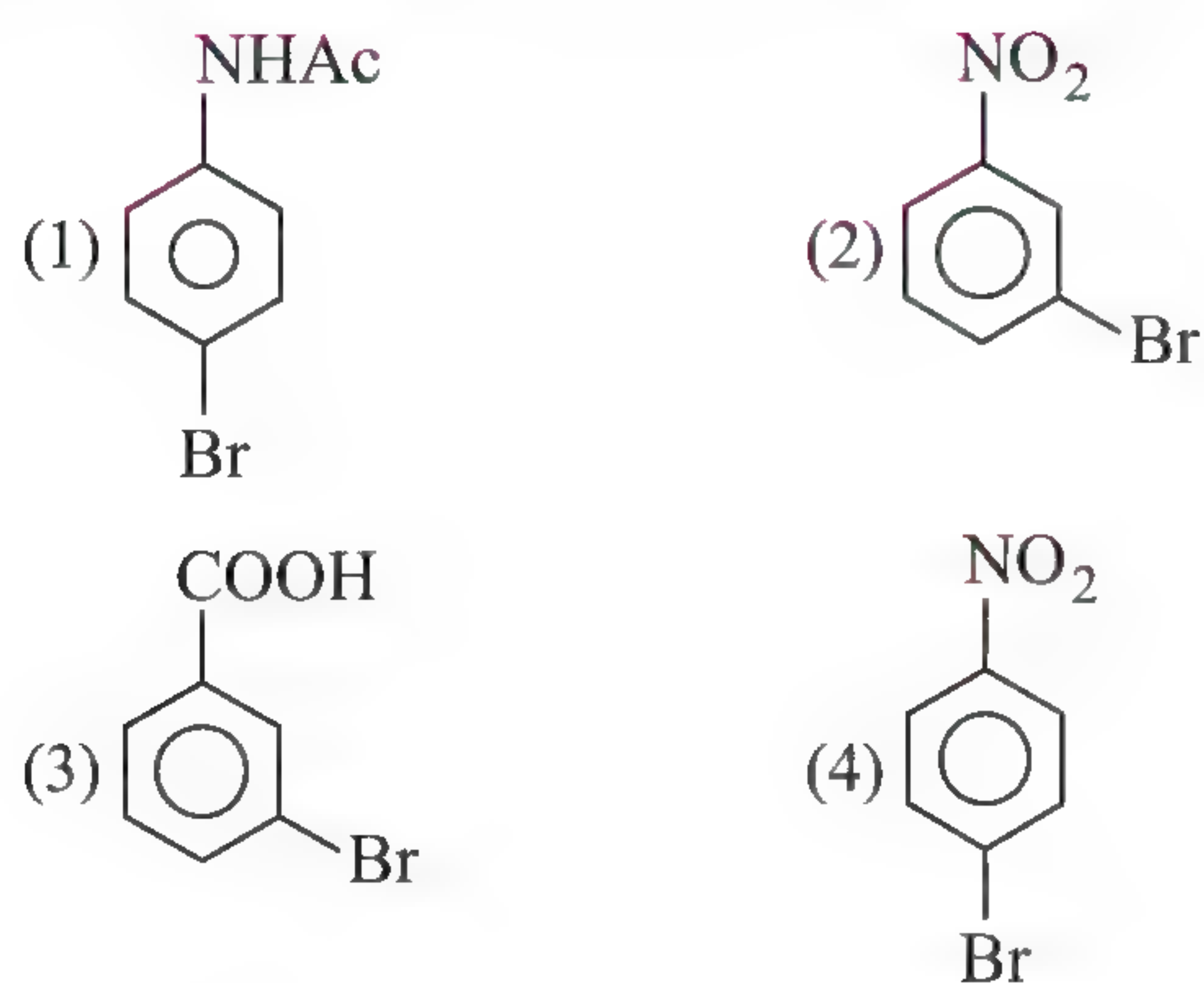
- (1) i. HBr + peroxide ii. Me_3CO^- , Δ iii. $\text{O}_3/\text{H}_2\text{O}$
 (2) i. HBr ii. $\text{C}_2\text{H}_5\text{O}^-$, Δ iii. $\text{O}_3/\text{H}_2\text{O}$
 (3) i. HI ii. MeO^- , Δ iii. $\text{O}_3/\text{Zn-acid}$
 (4) HCl + peroxide



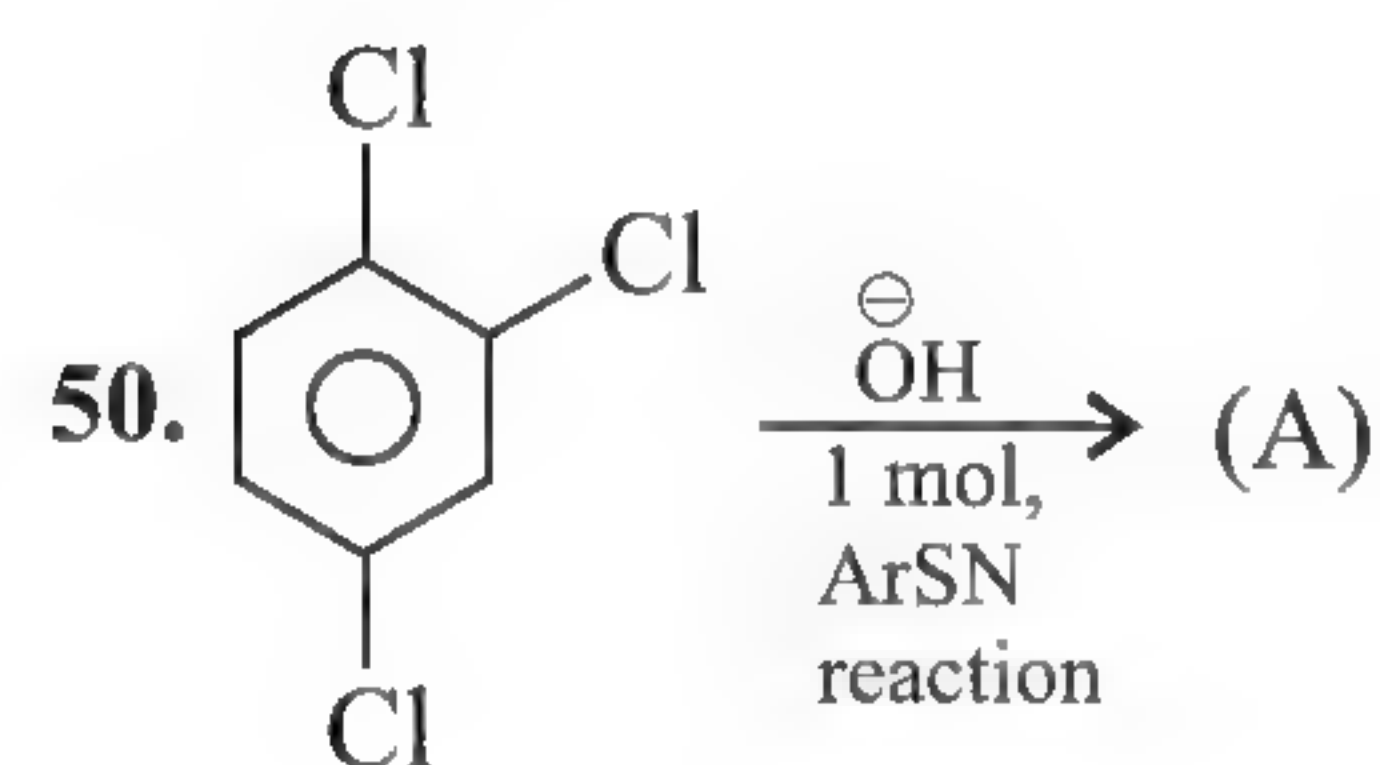
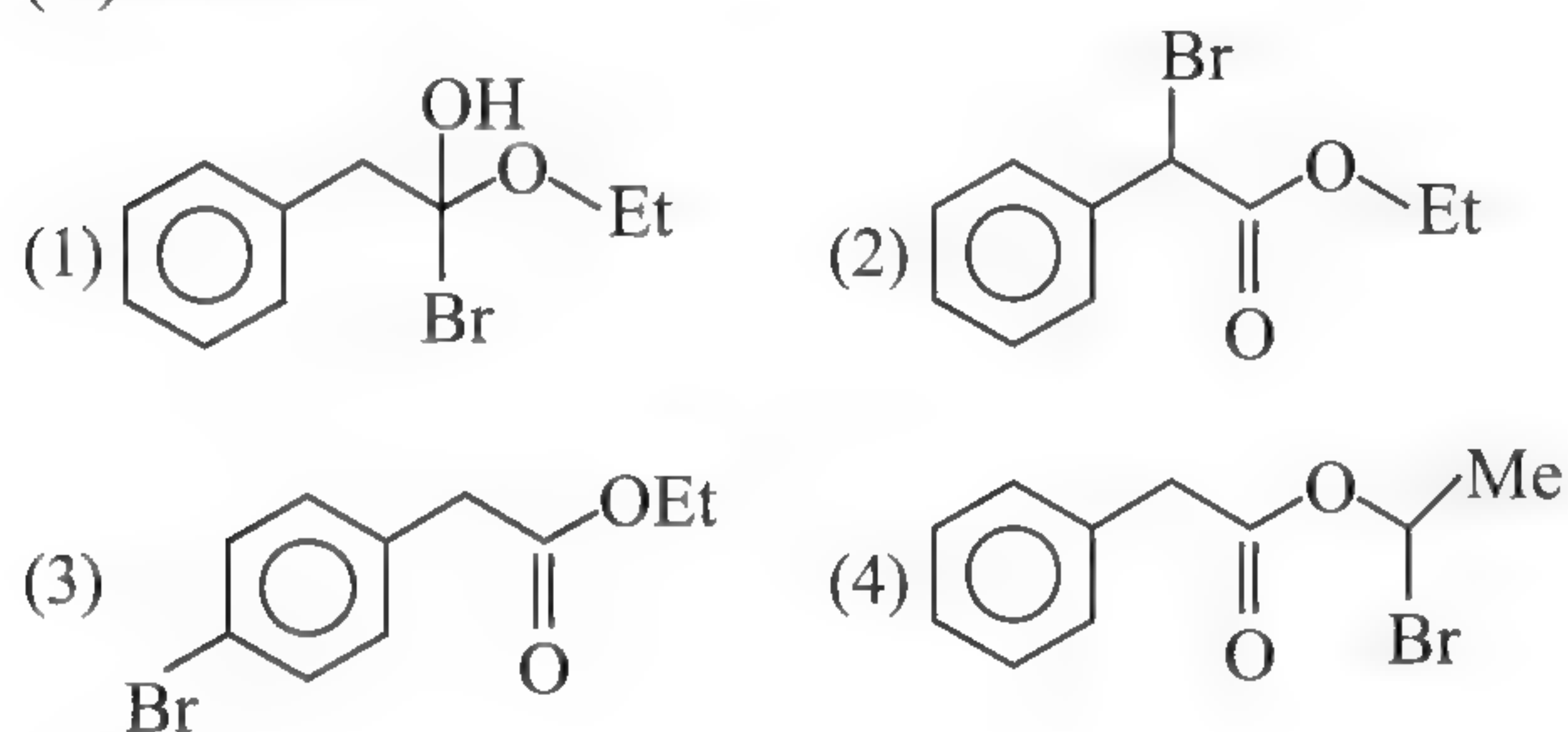
Product (C) is:



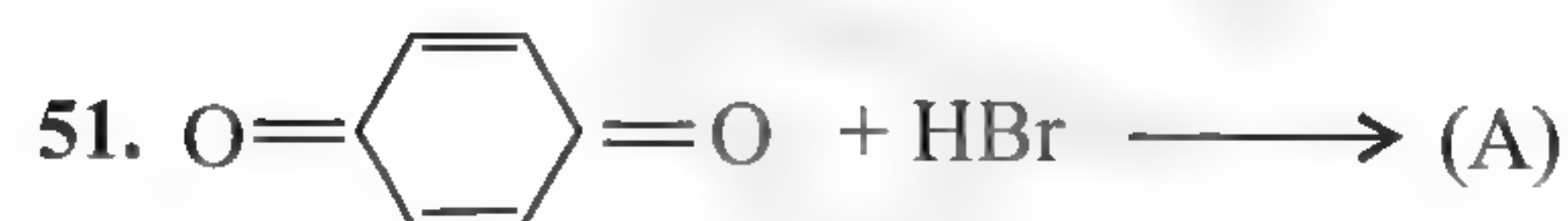
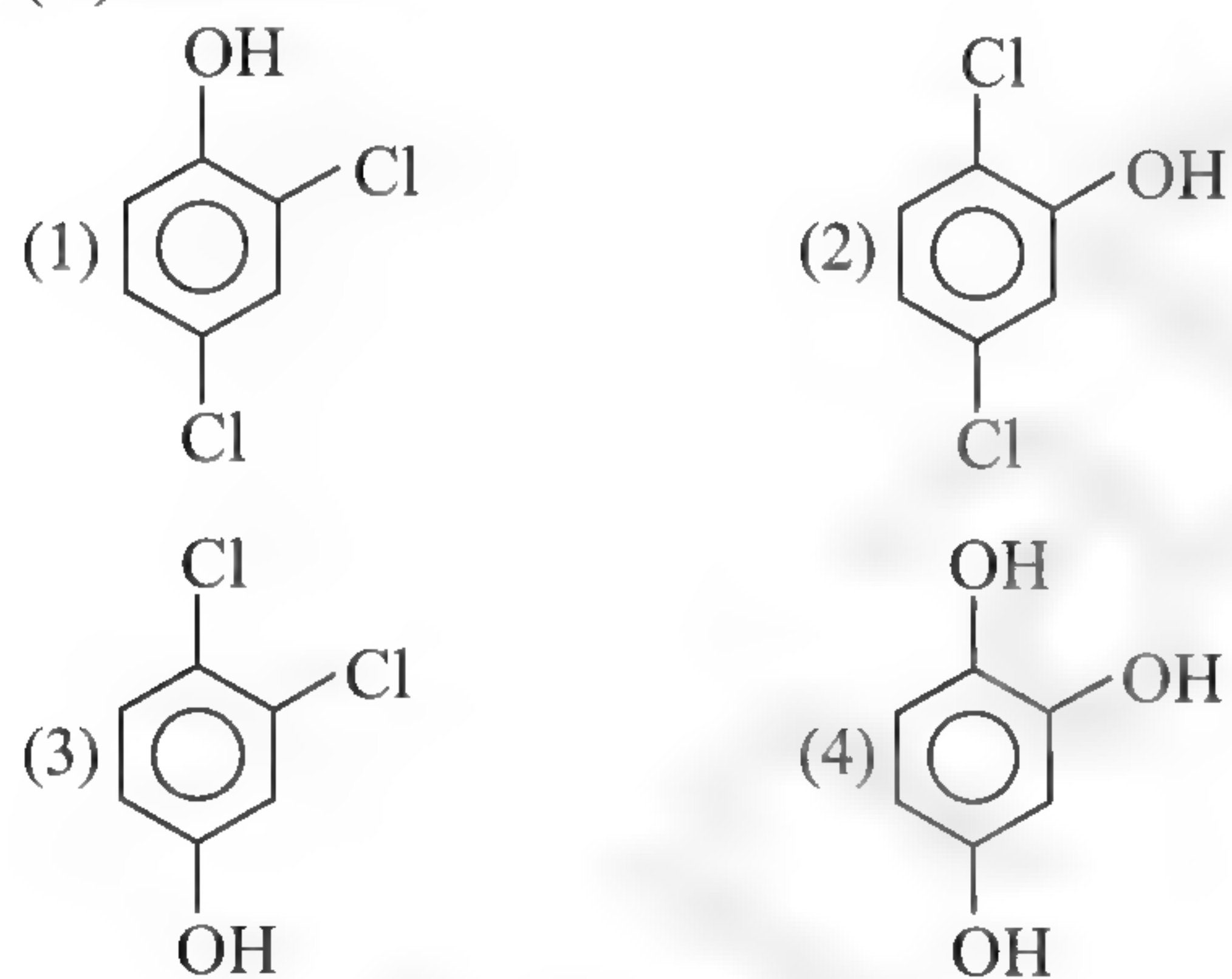
(D) would be:



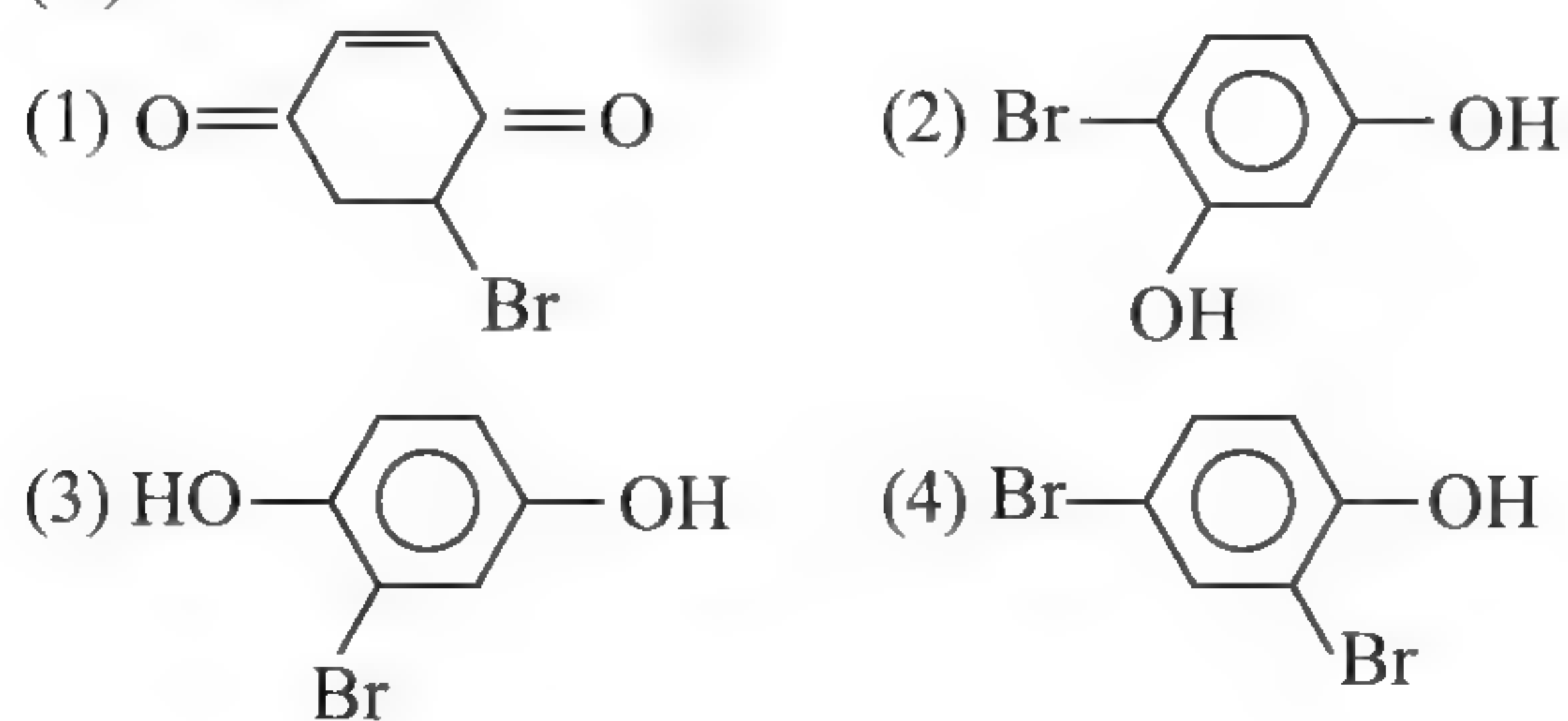
(A) would be:



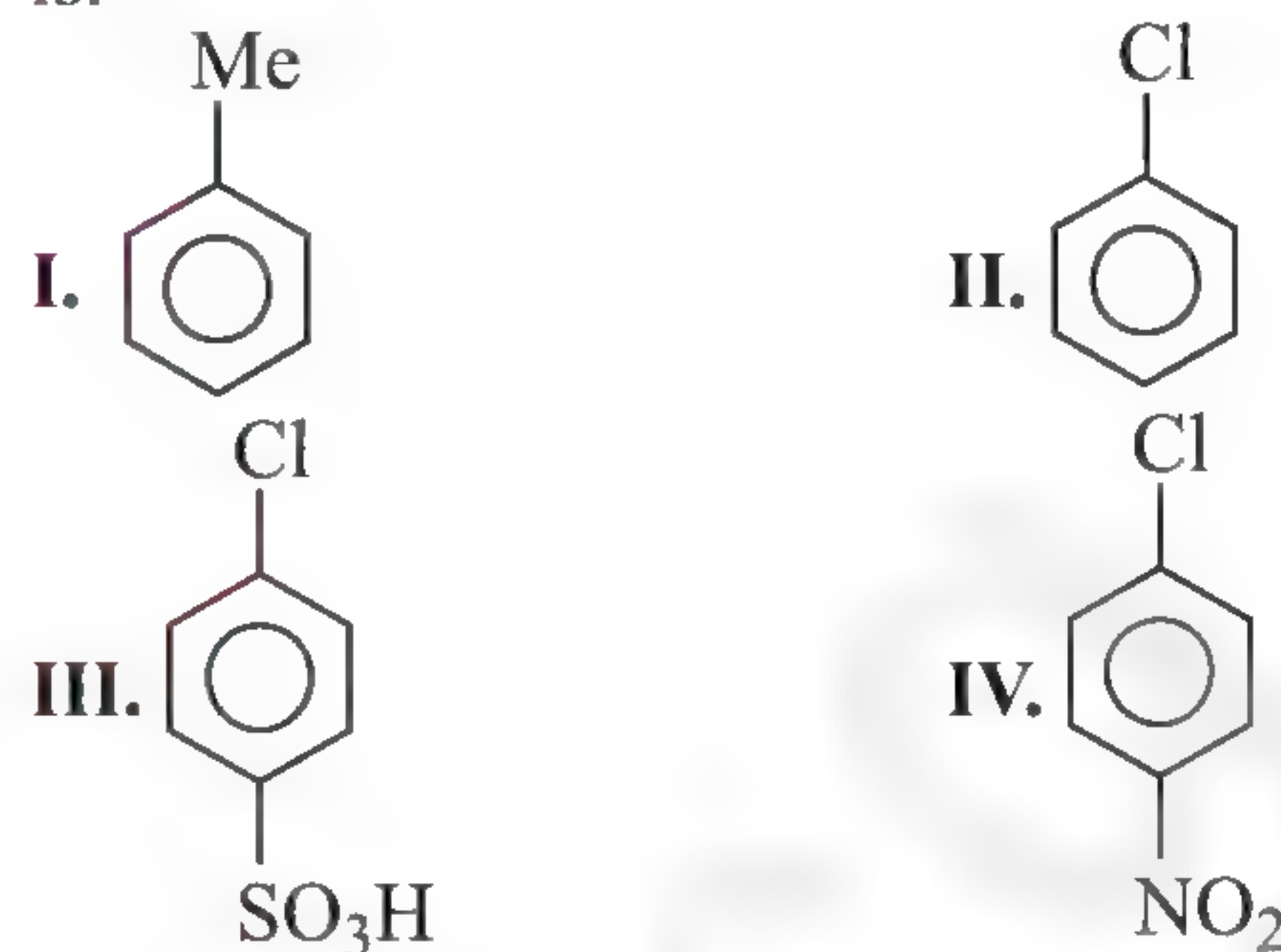
(A) would be:



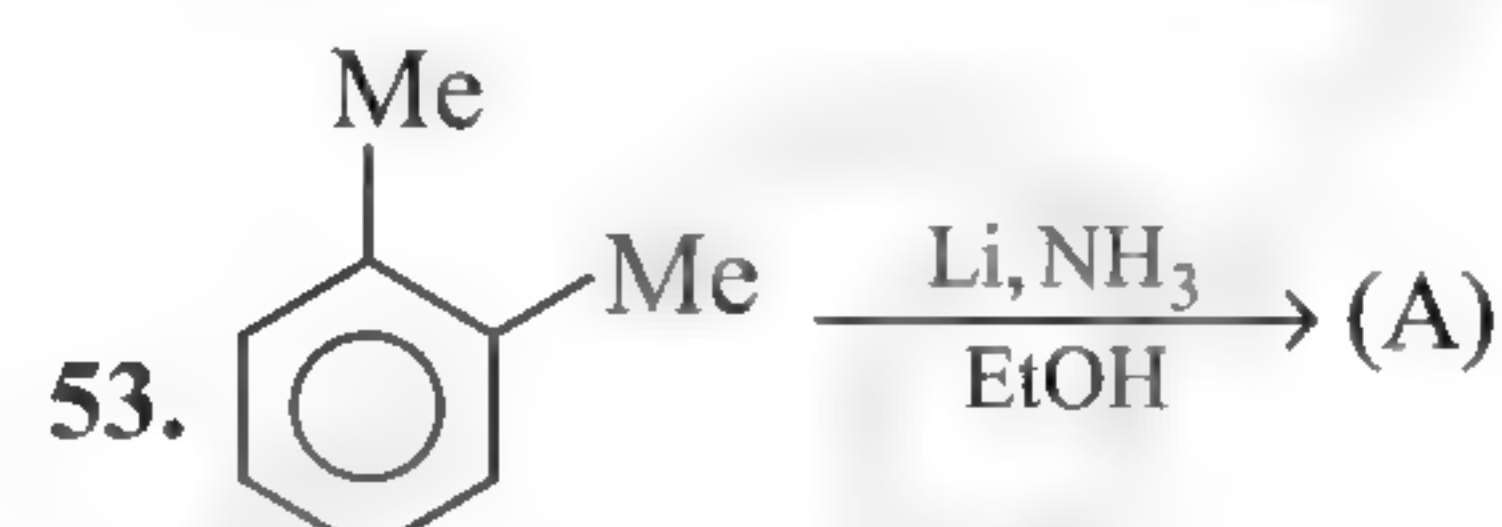
(A) would be:



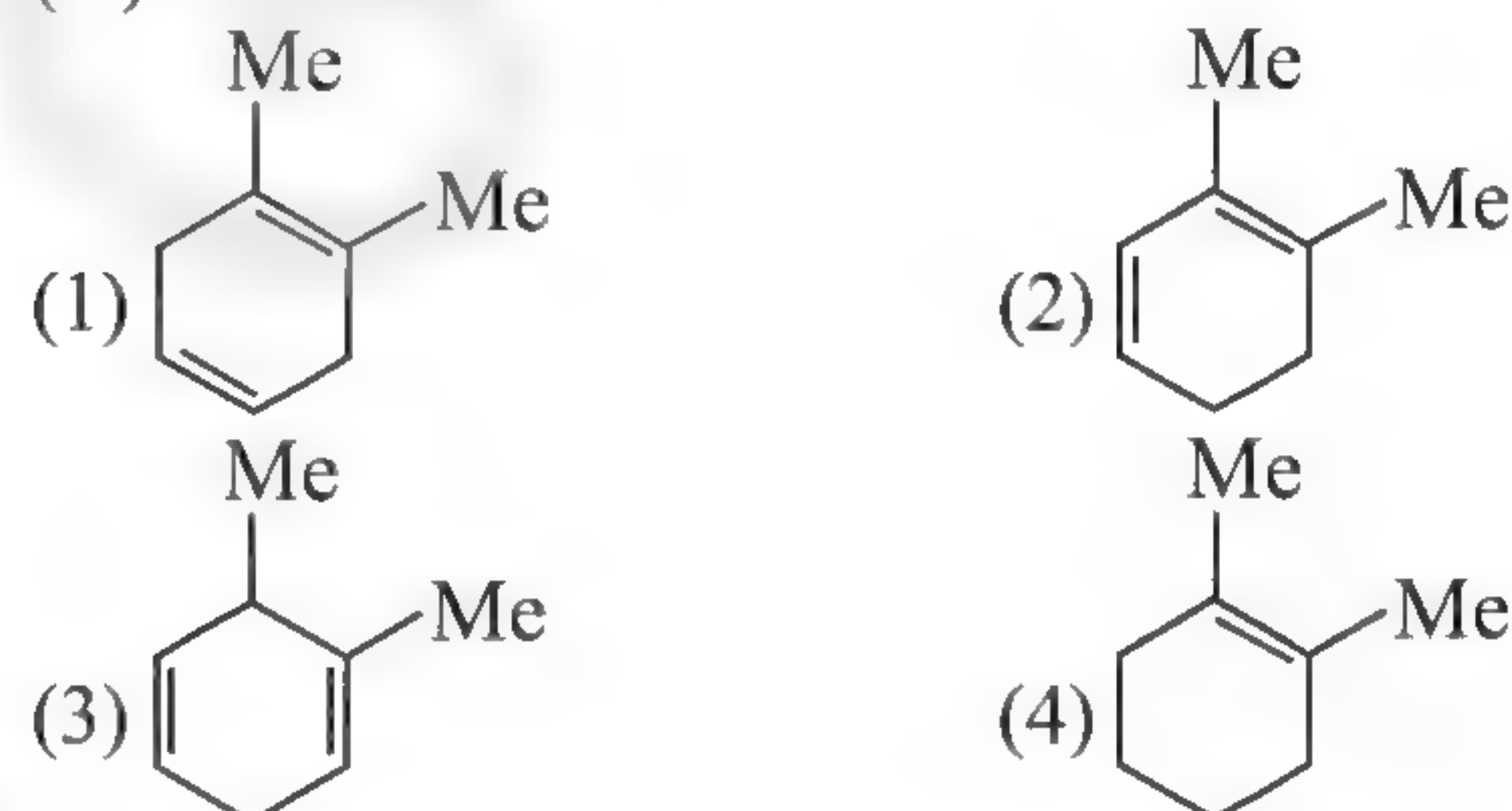
52. The decreasing order of ArSN reaction with $\text{C}_2\text{H}_5\text{O}^-/\text{EtOH}$ is:



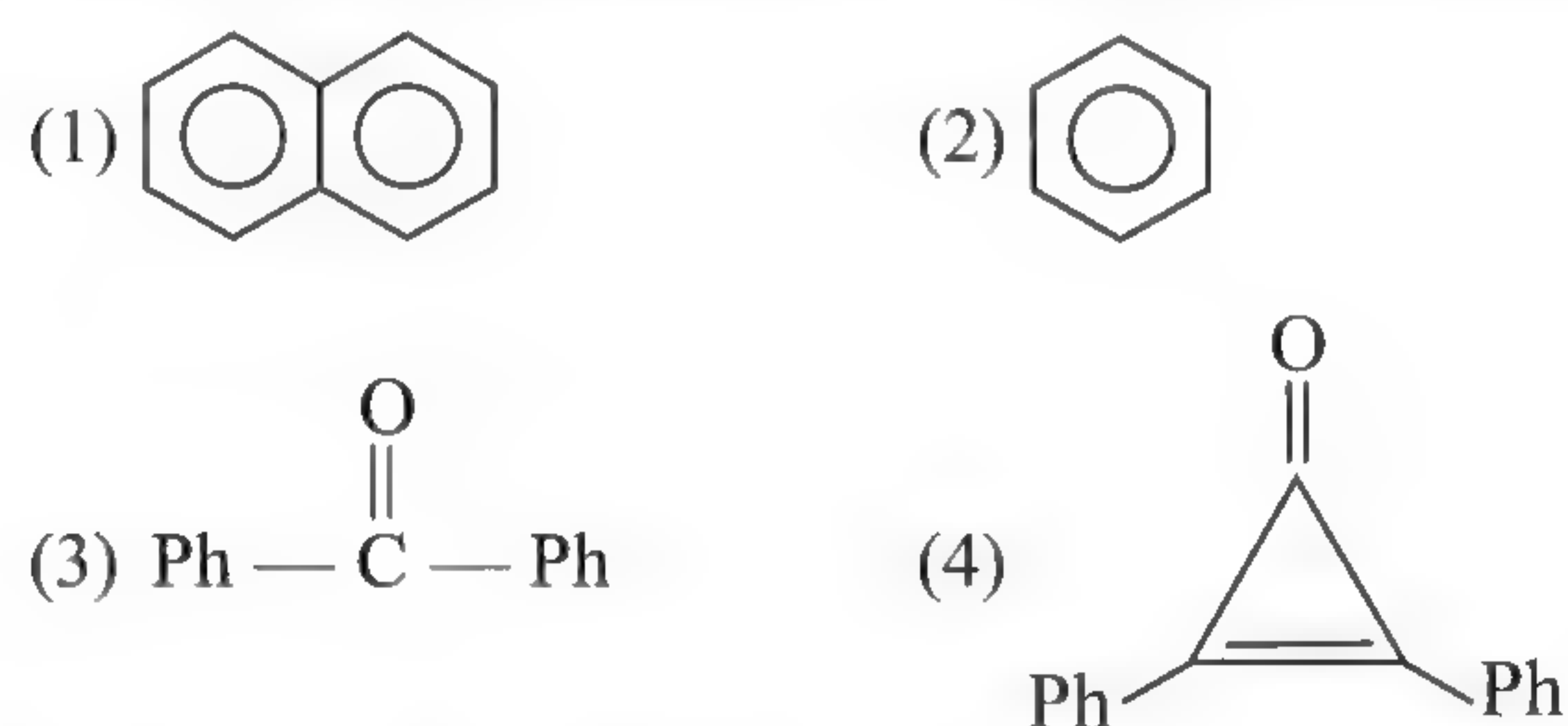
- (1) (I) > (II) > (III) > (IV) (2) (IV) > (III) > (II) > (I)
(3) (III) > (IV) > (II) > (I) (4) (IV) > (III) > (I) > (II)



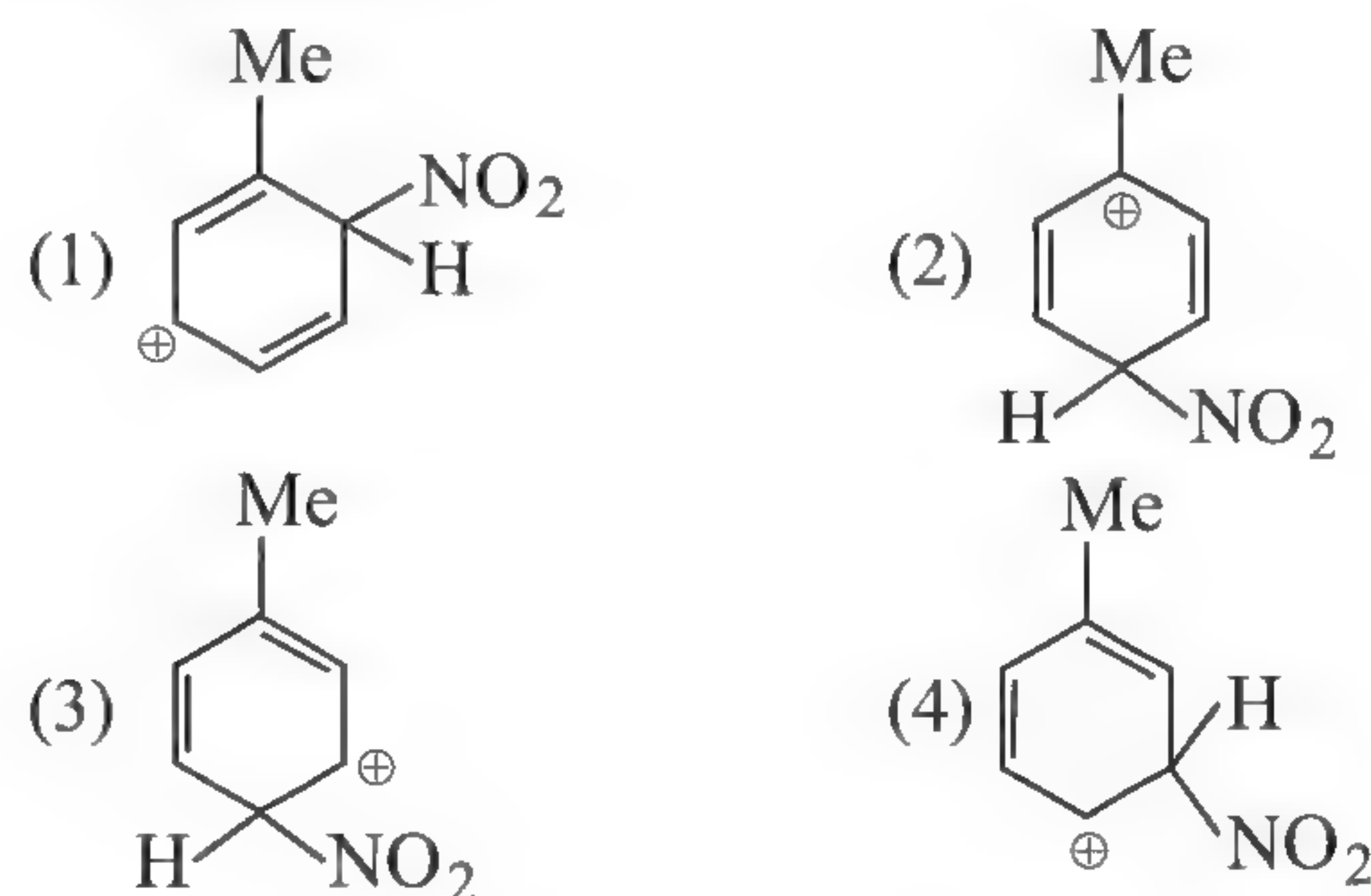
(A) would be:



54. Which of the following has the highest dipole moment?

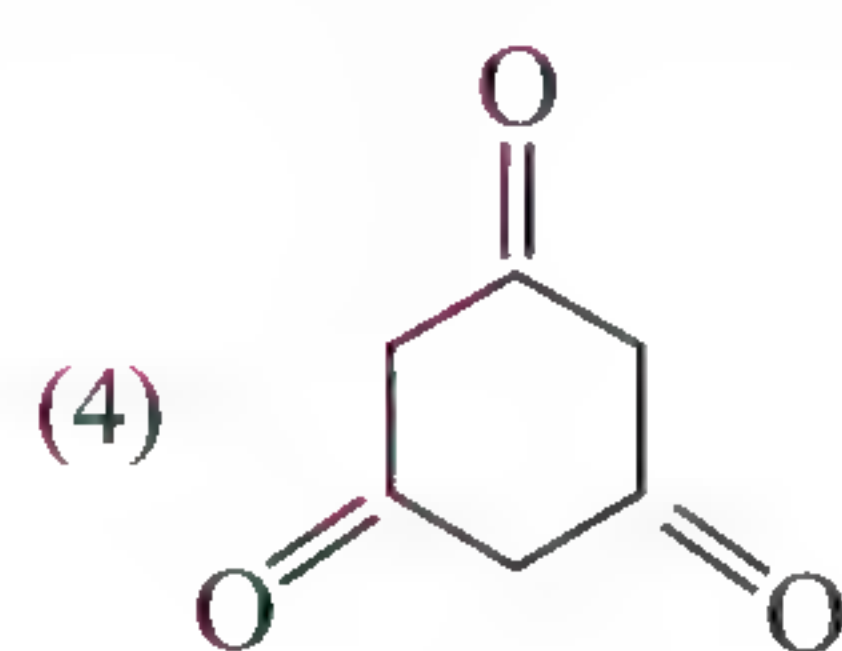
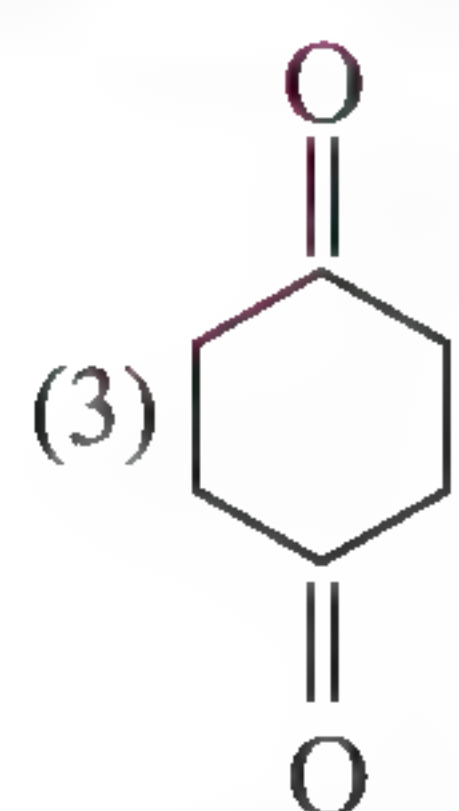


55. Which of the following is the most stable arenonium or benzenium ion?

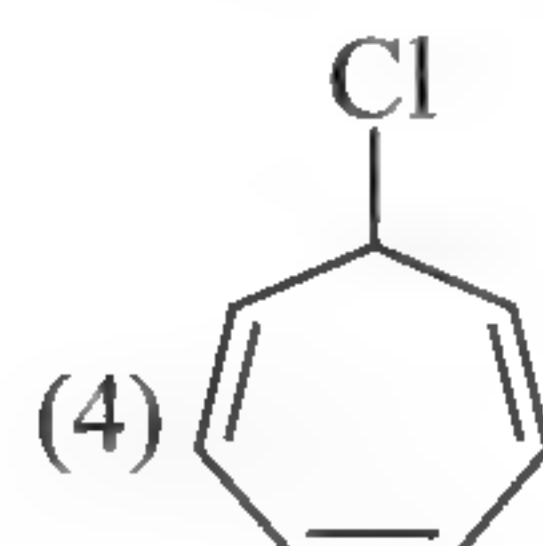
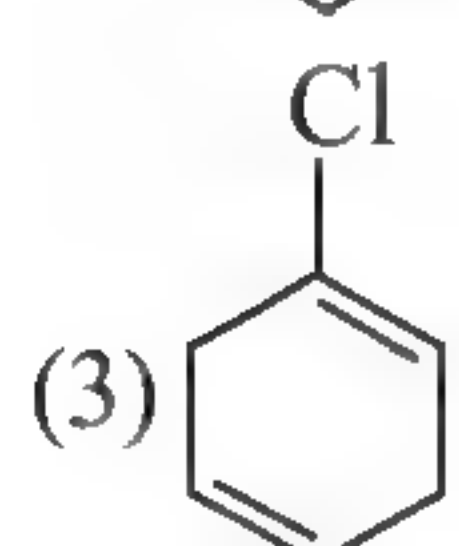
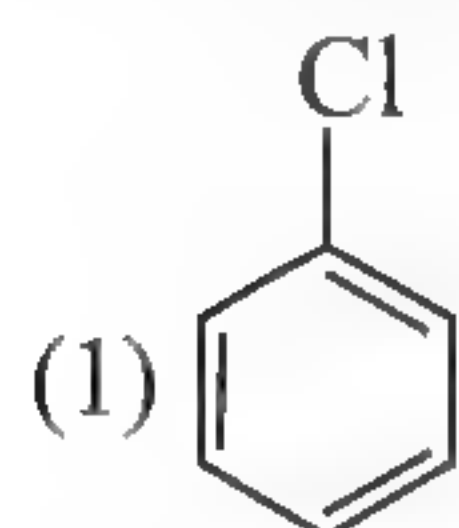


56. Which of the following ketonic compound is the least stable?

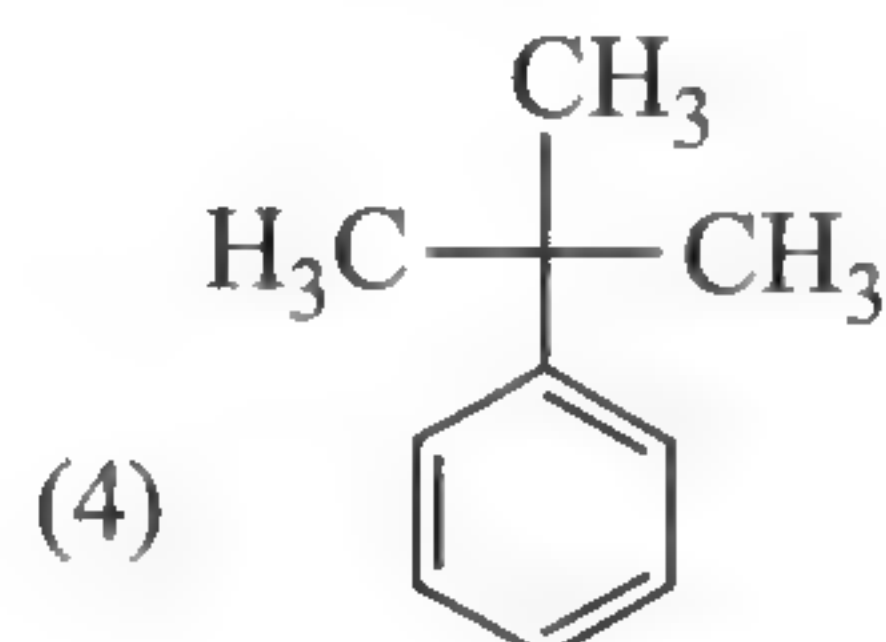
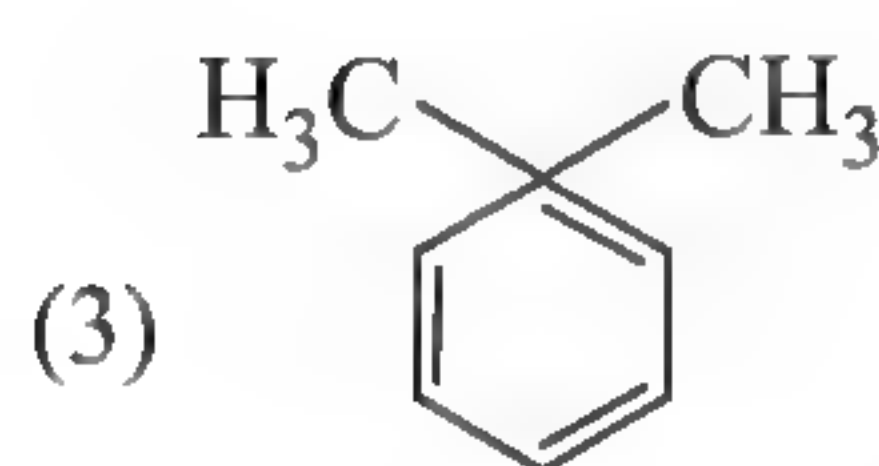
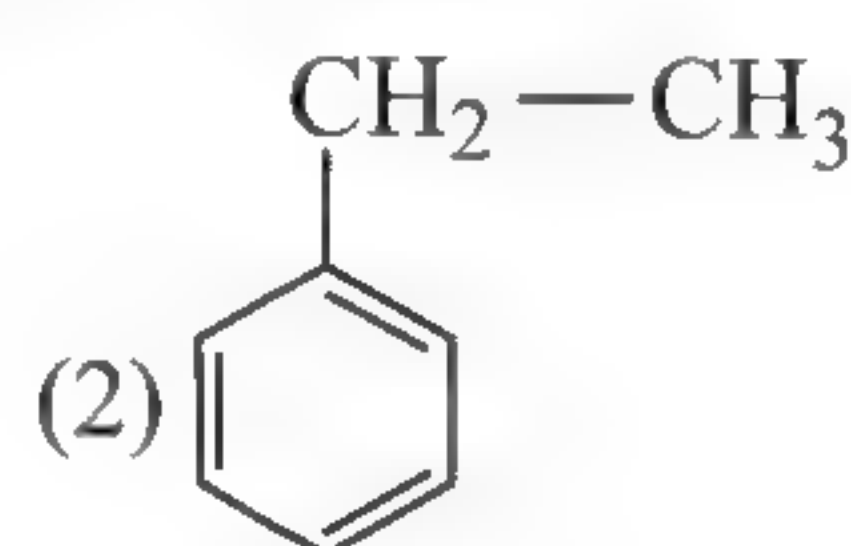
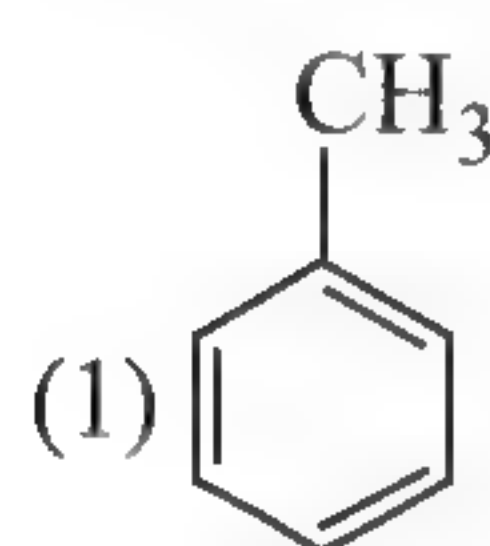




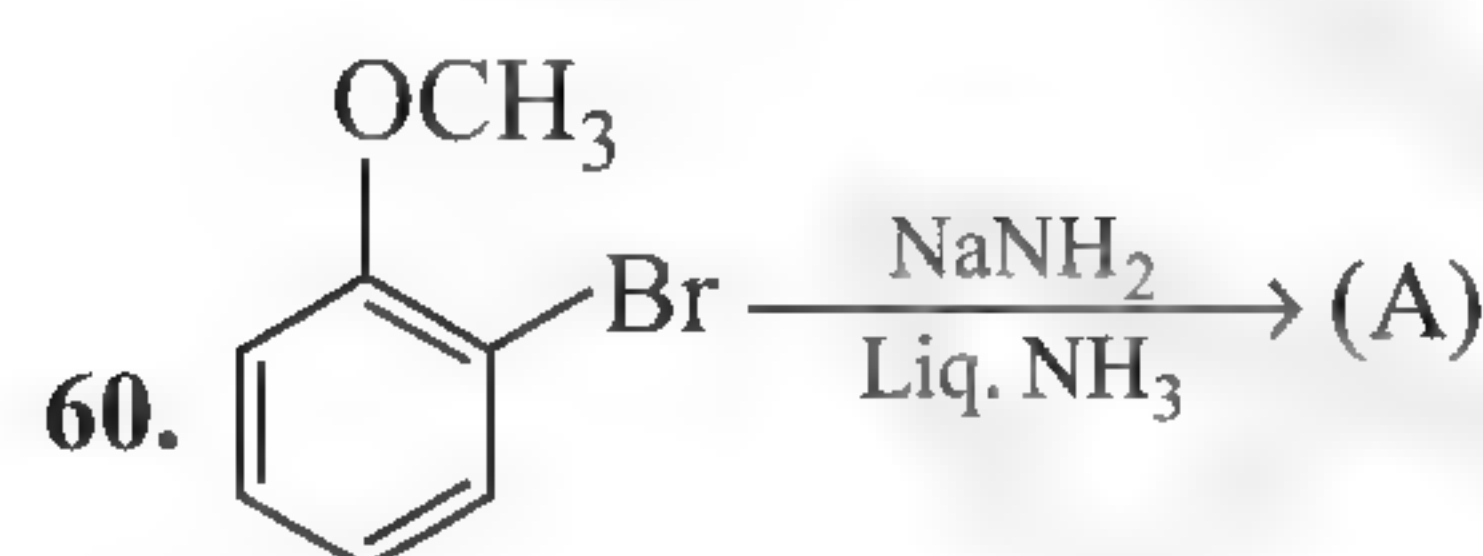
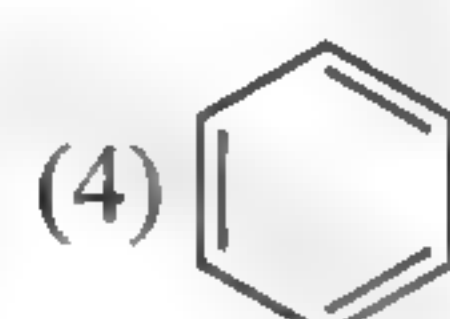
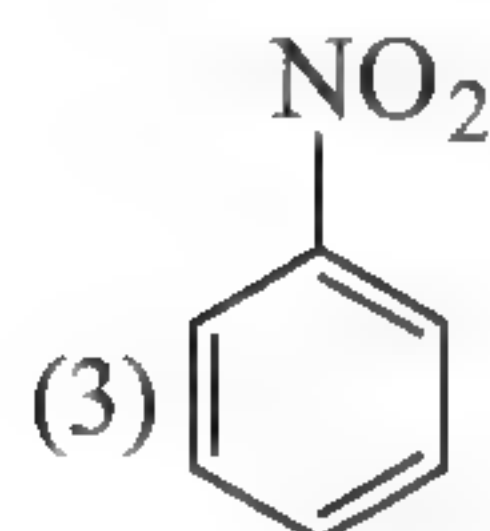
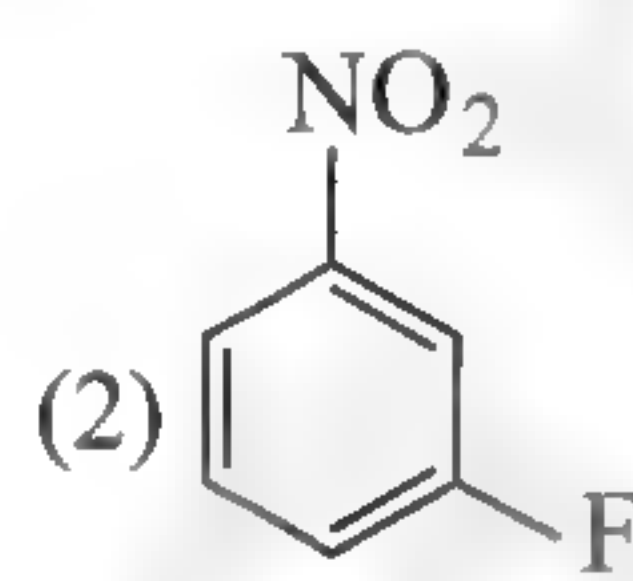
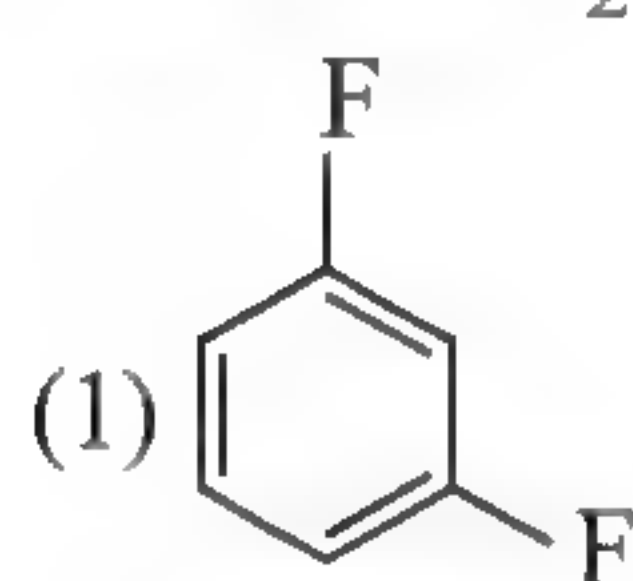
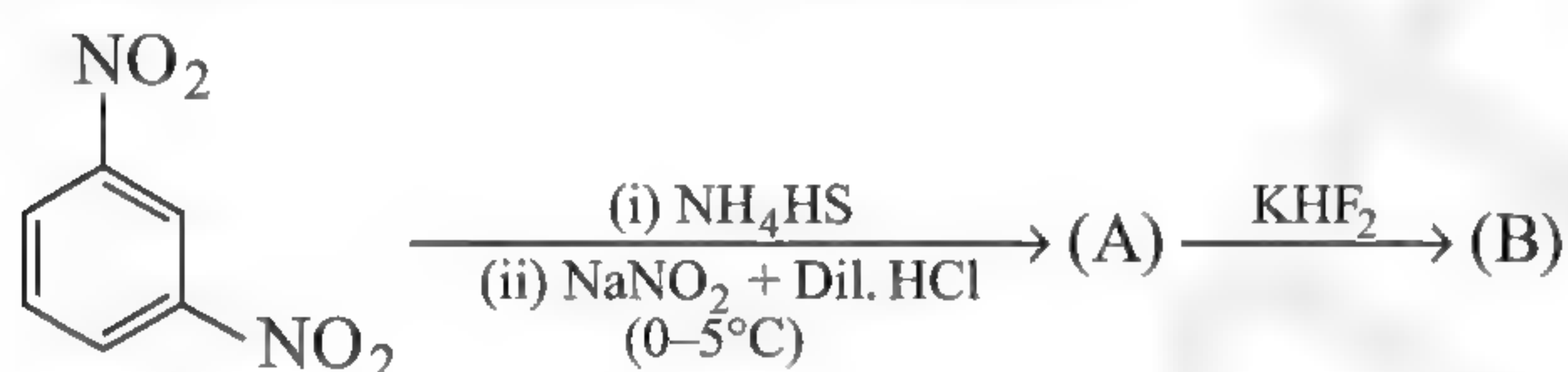
57. Which of the following compounds will give curdy precipitate with AgNO_3 solution?



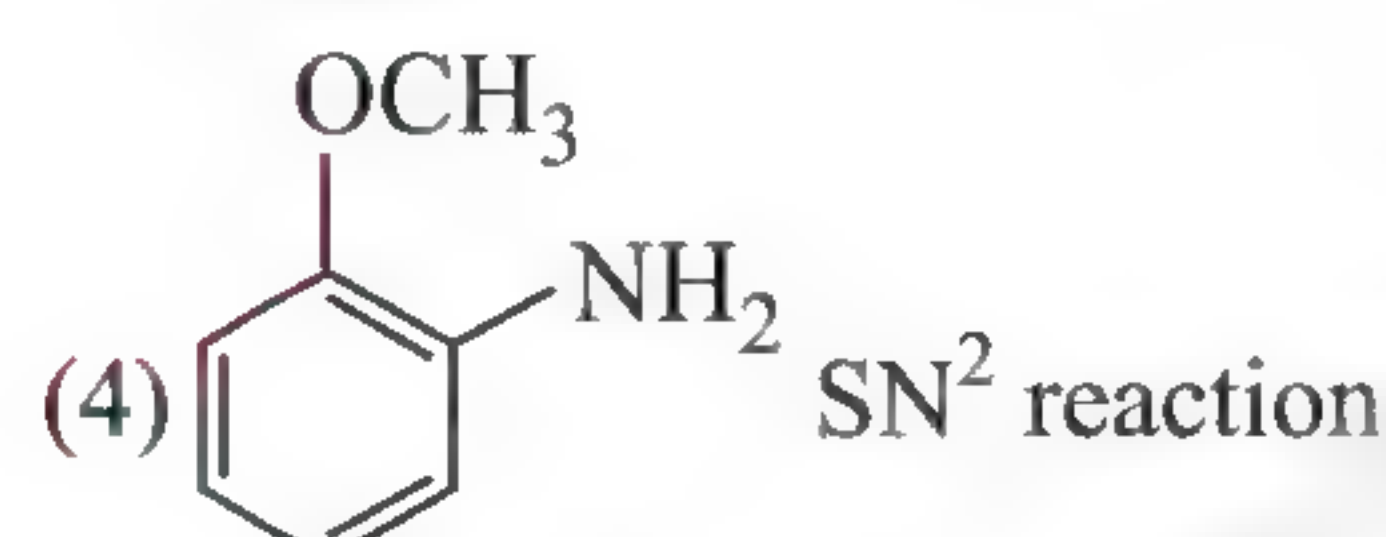
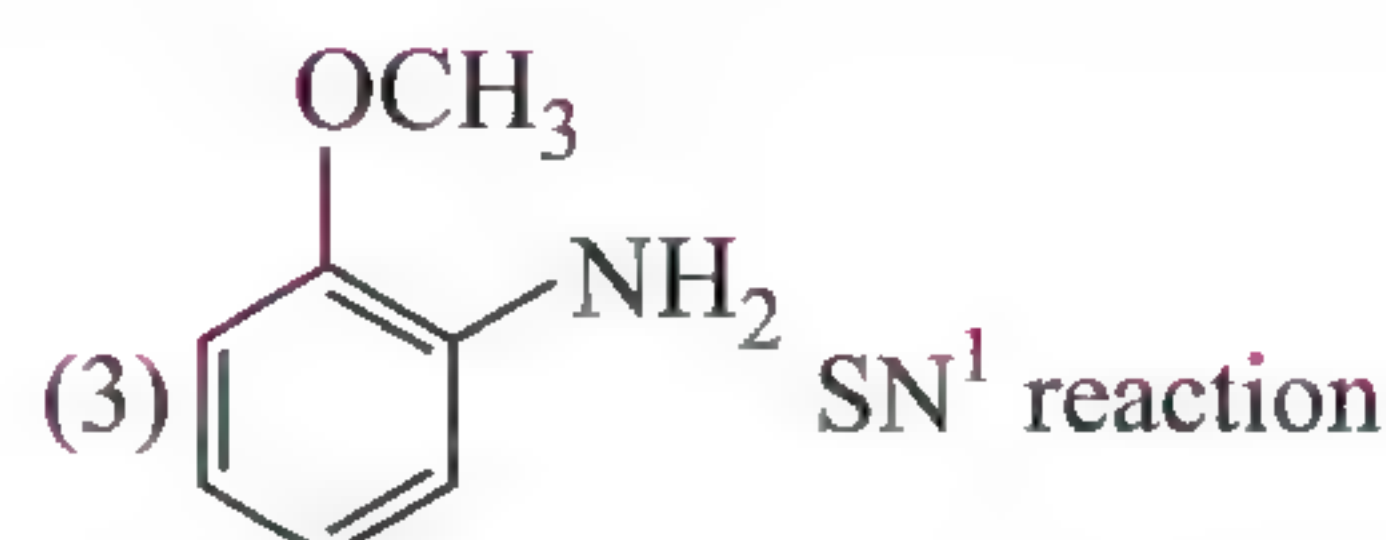
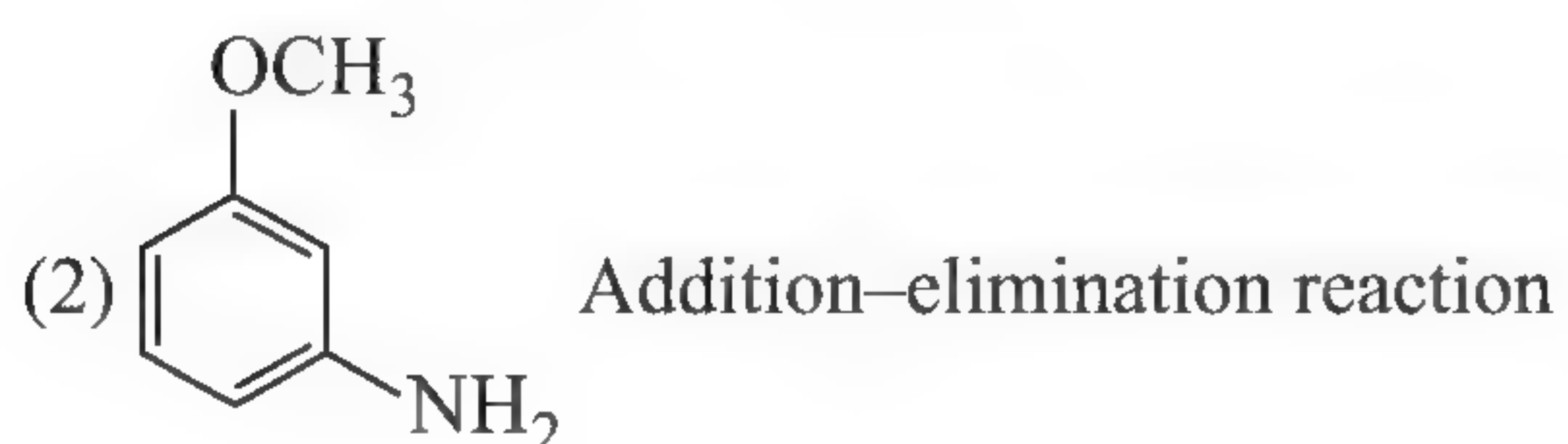
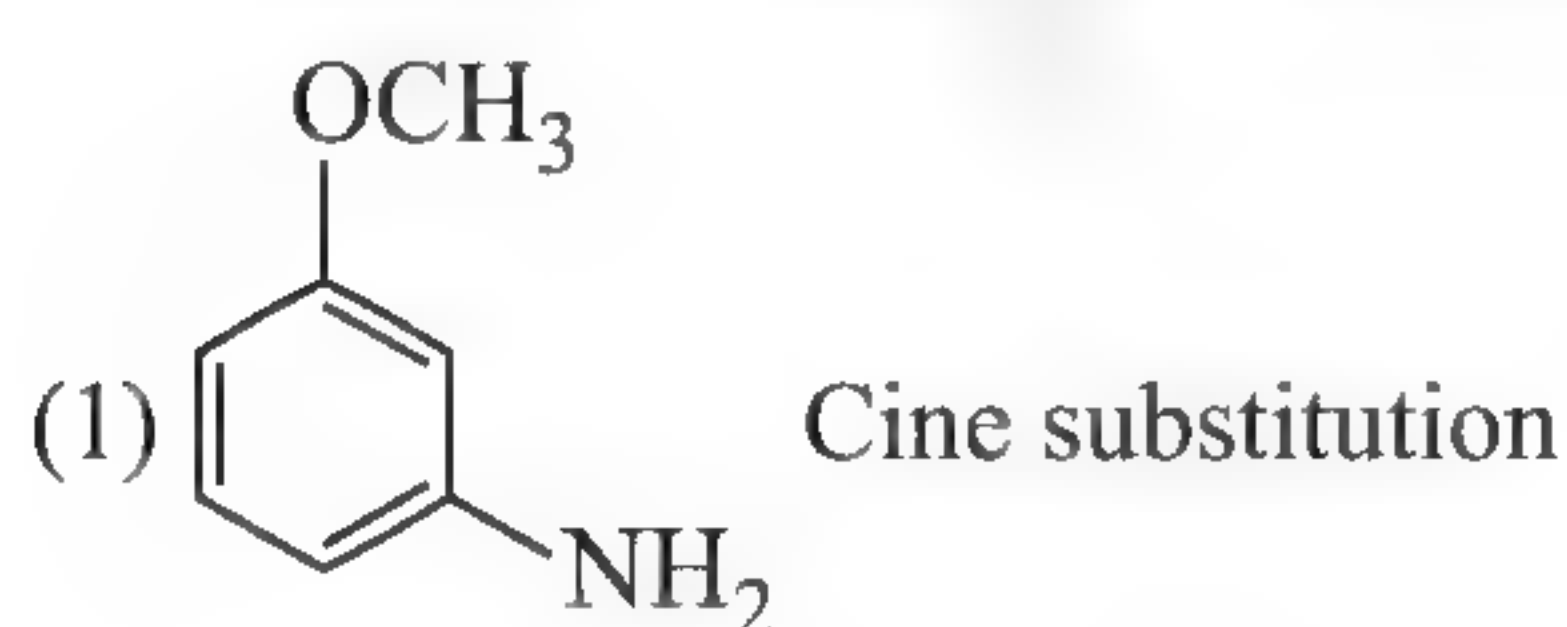
58. Which of the following compounds is the most reactive towards electrophilic substitution reaction?



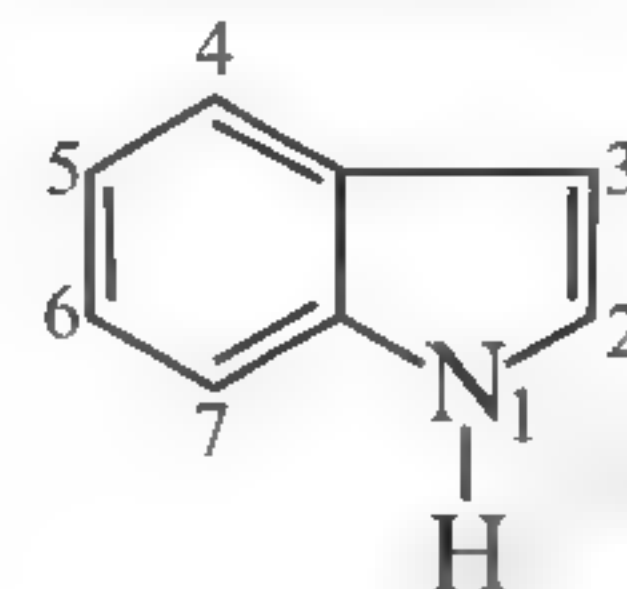
59. What is the end product of the reaction?



The major product (A) and reaction R are:



61. Which of the following mentioned positions in the given compound is more reactive towards electrophilic substitutions?



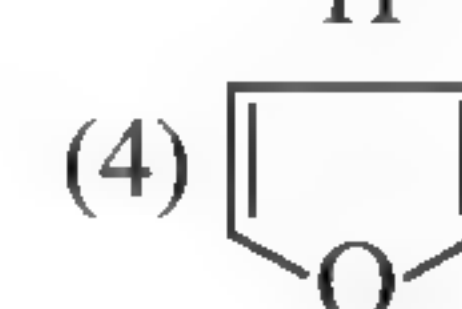
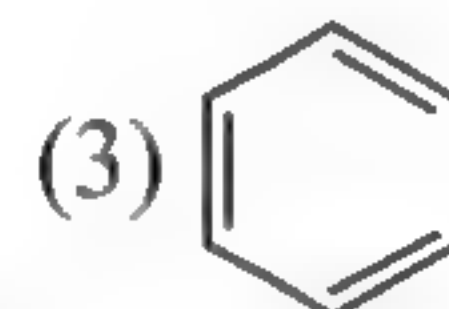
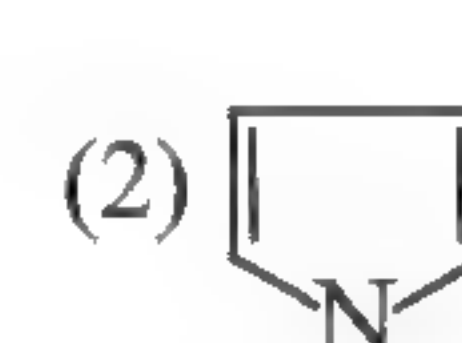
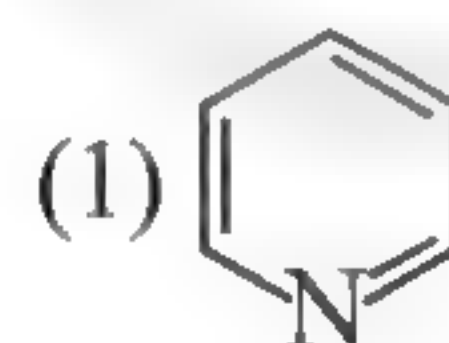
(1) 3

(2) 2

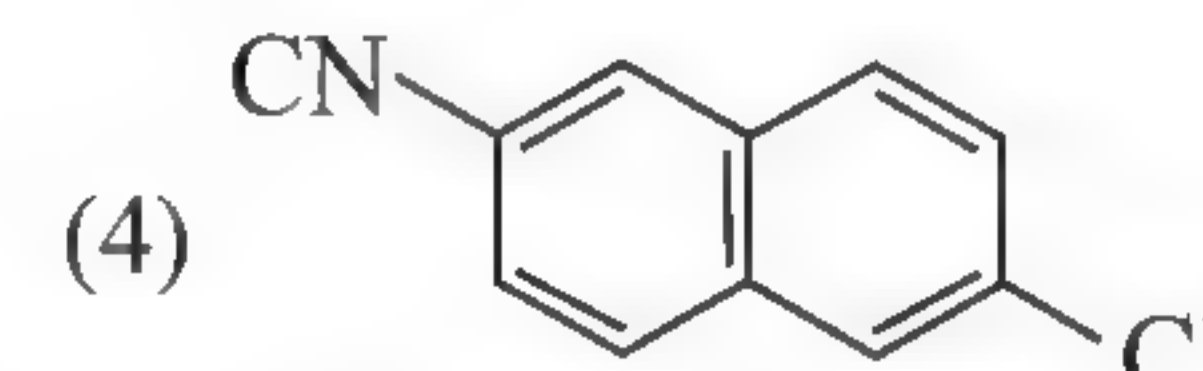
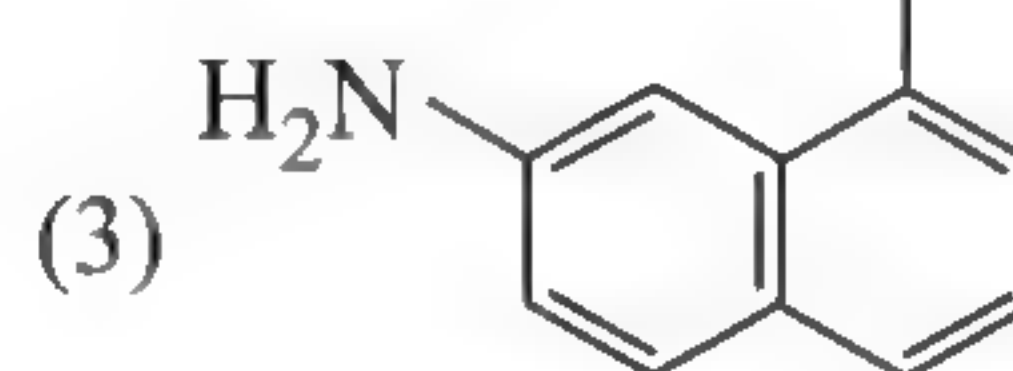
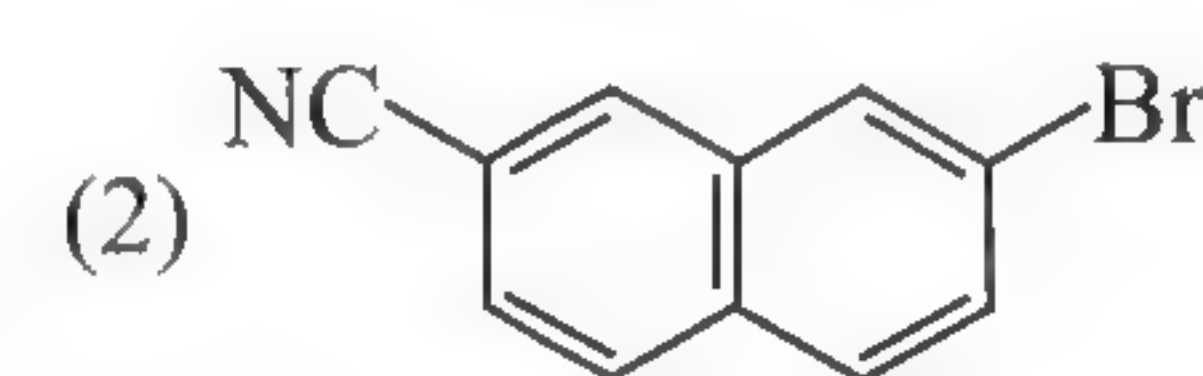
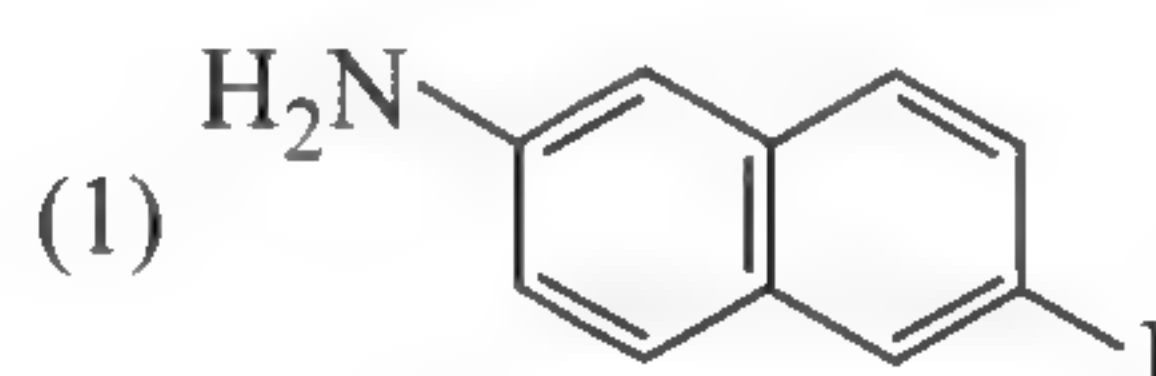
(3) 5

(4) 6

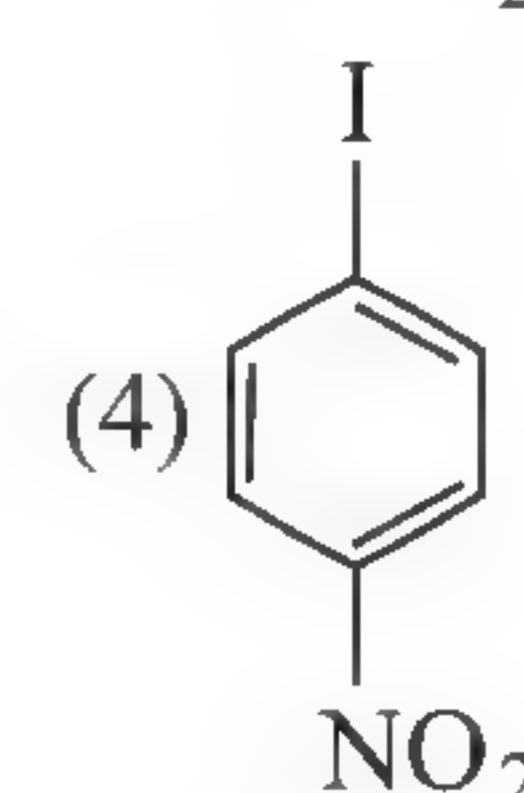
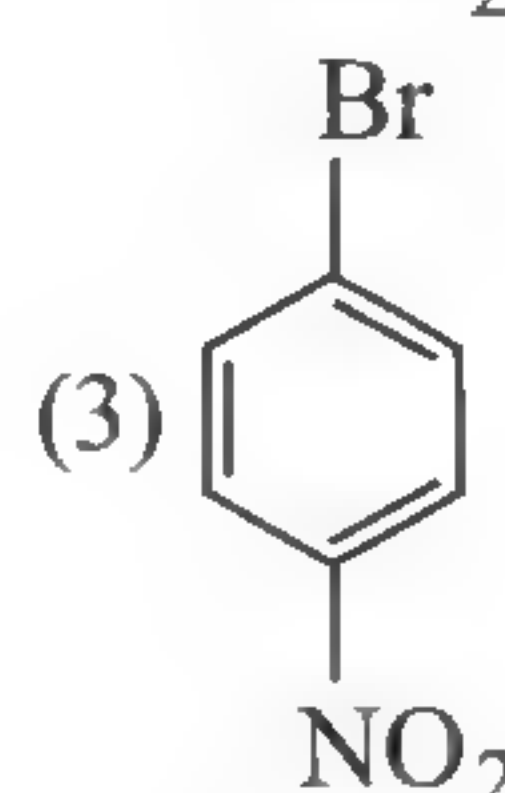
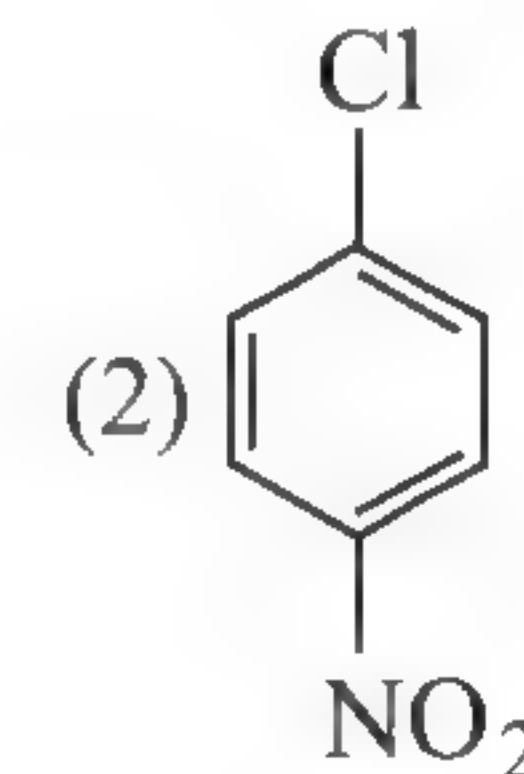
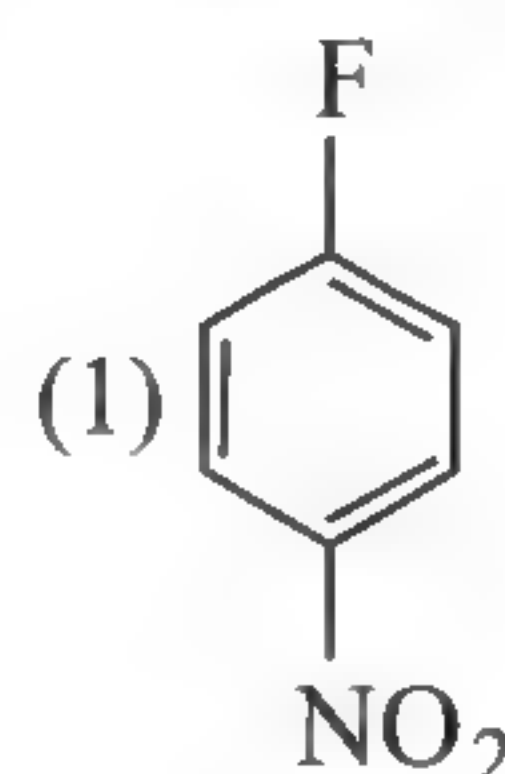
62. Which of the following aromatic compounds is the least reactive towards electrophilic substitutions?



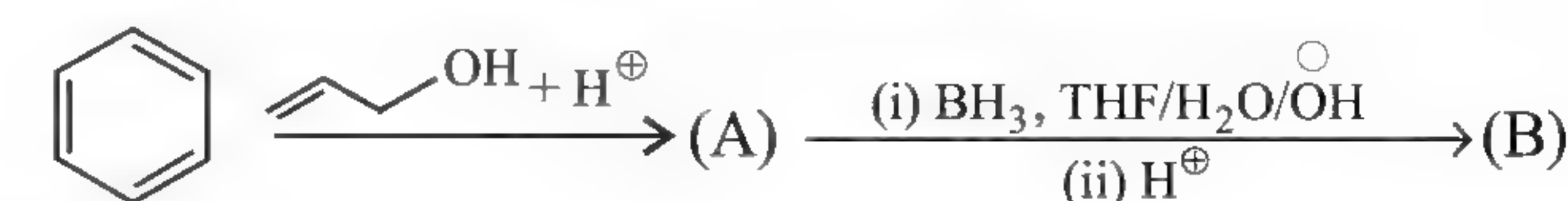
63. In the reaction product (P) will be:

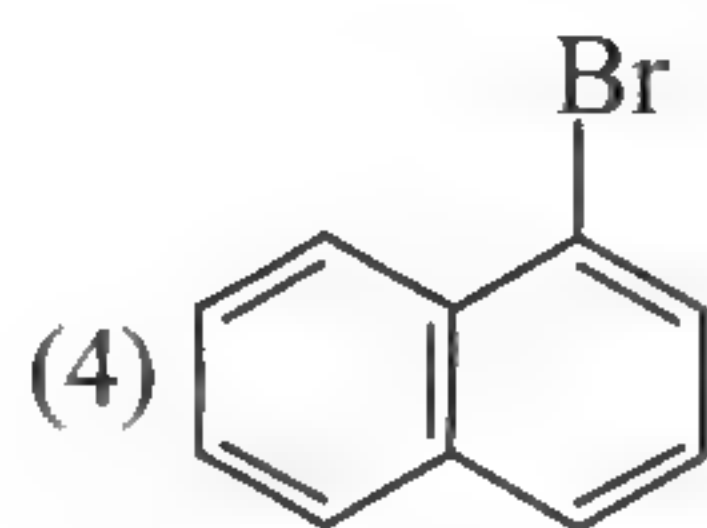
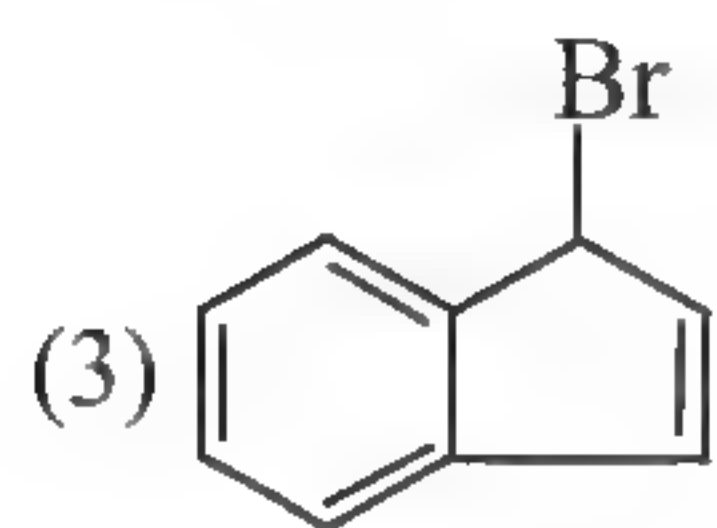
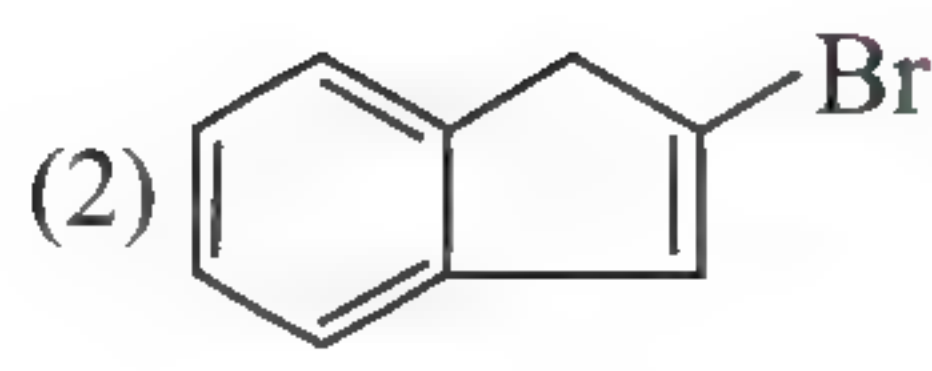
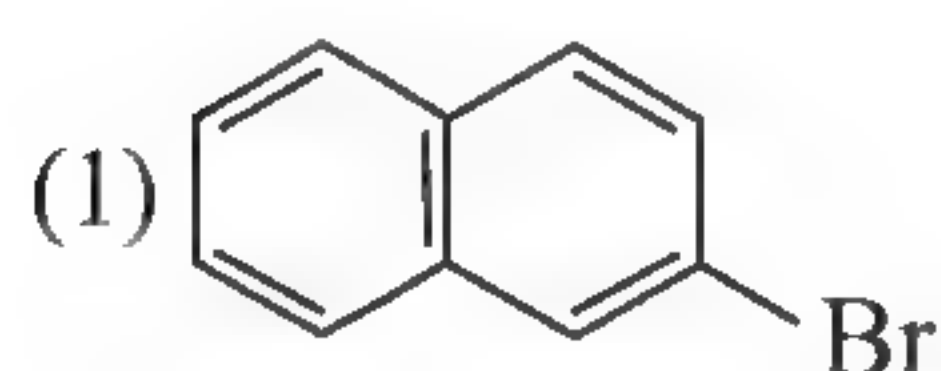


64. Which of the following compounds will show faster ArSN^2 reaction?

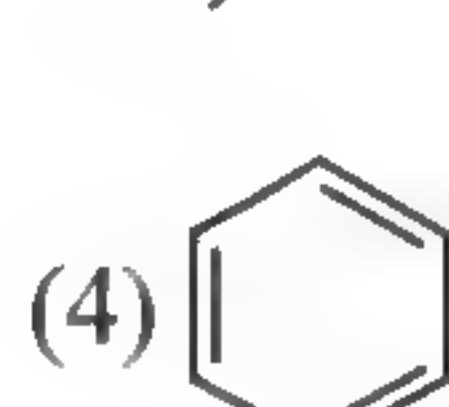
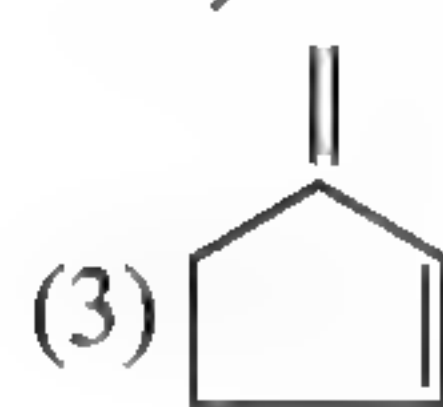
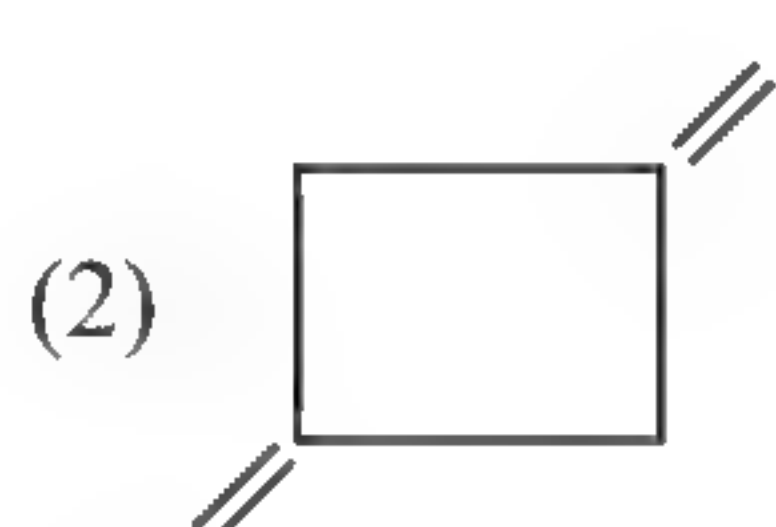
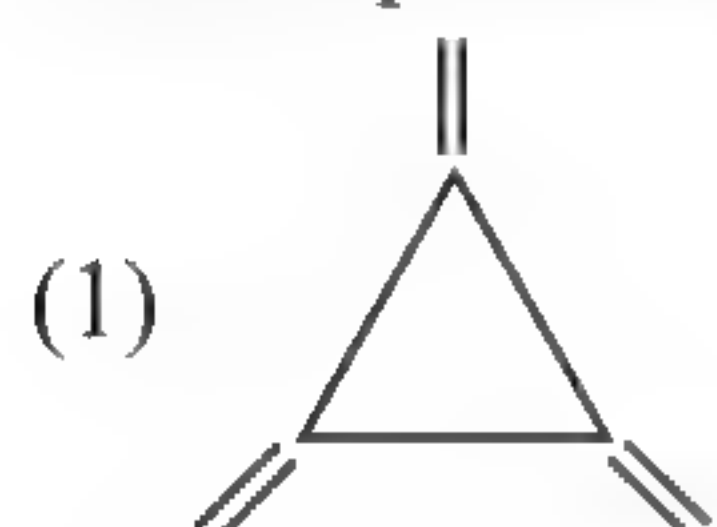
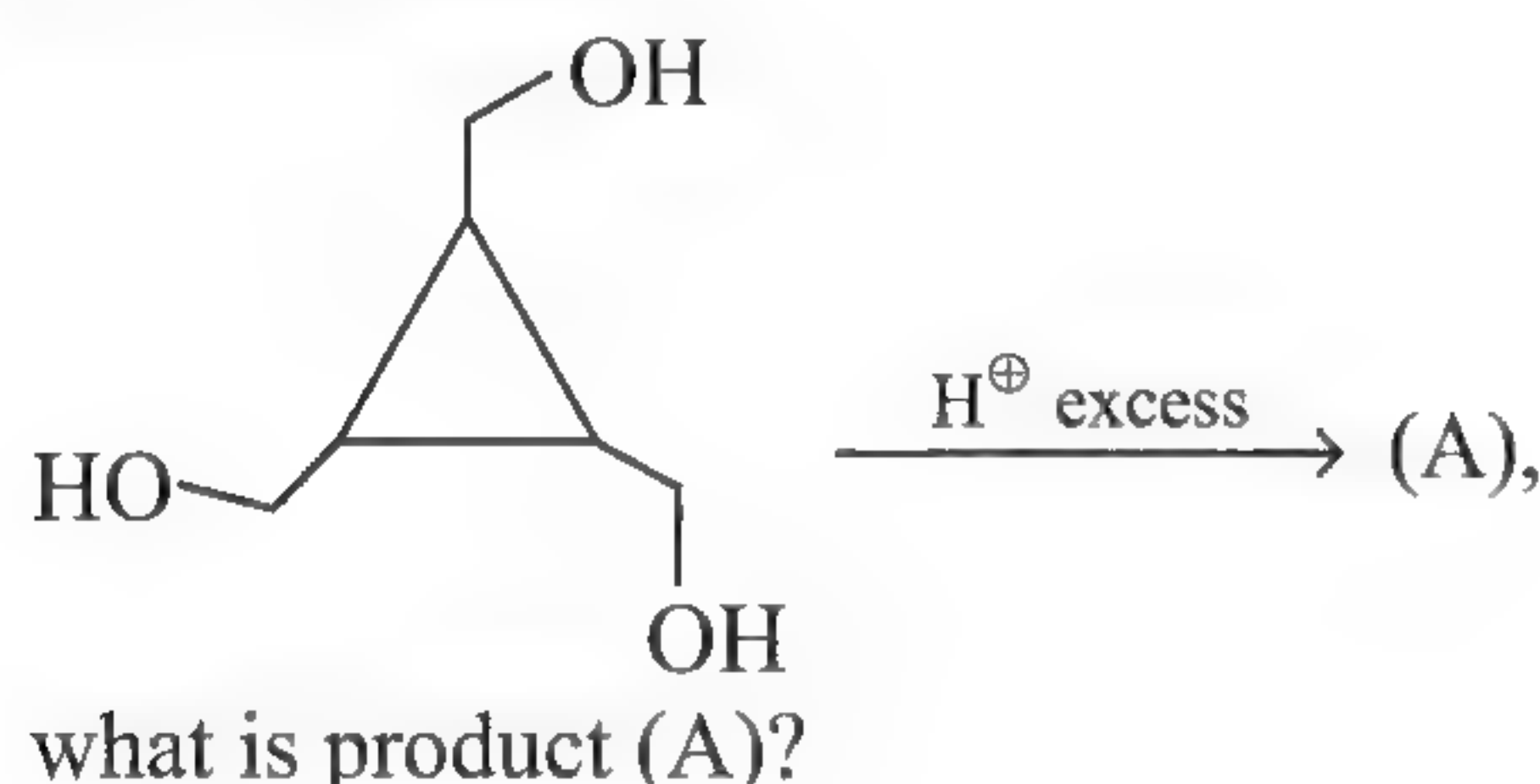


65. What is the end product (D) of the following reaction?

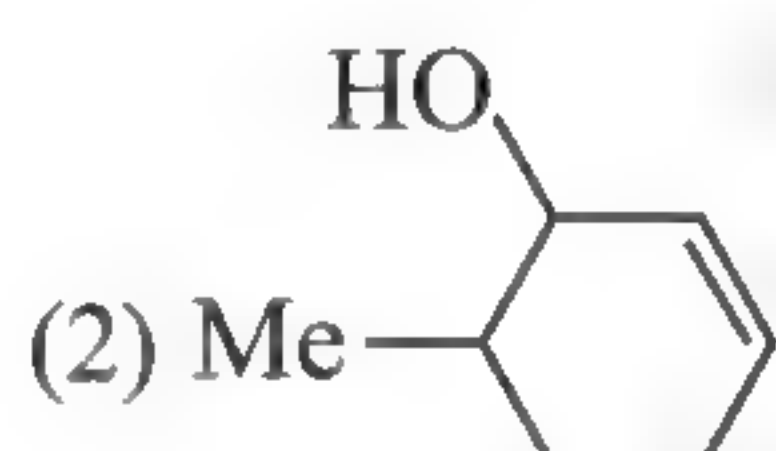
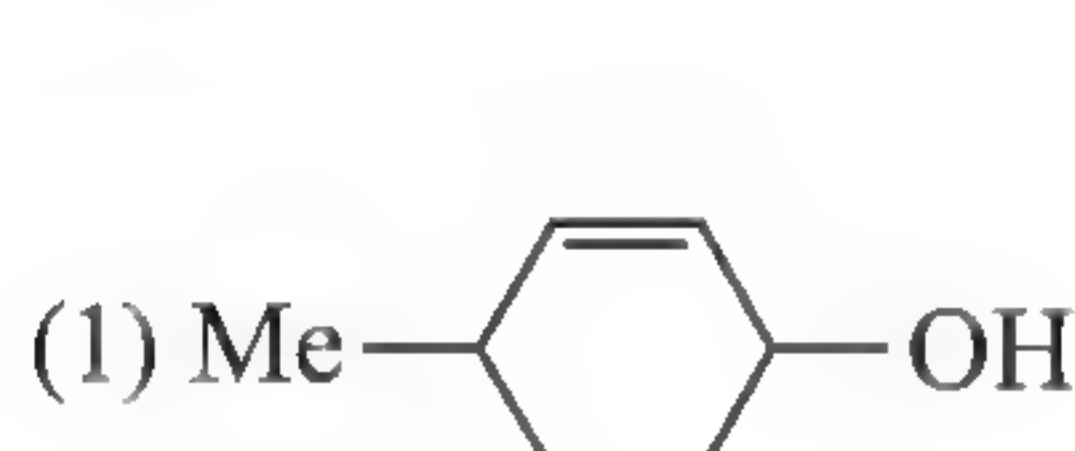




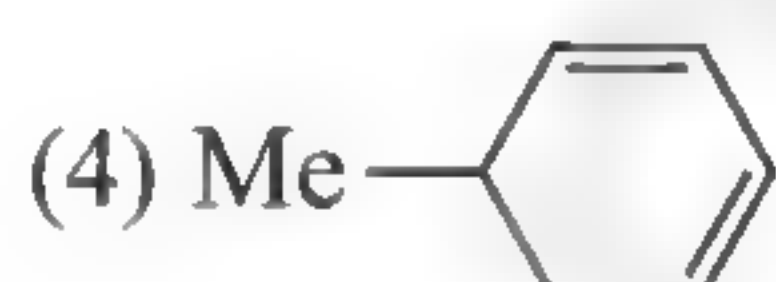
66. For the reaction:



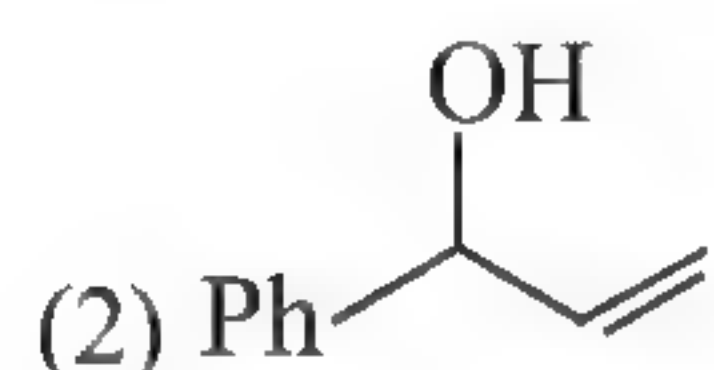
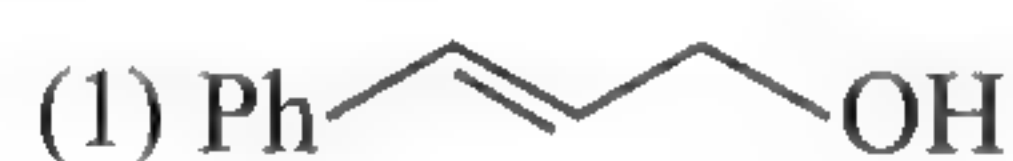
67. In the reaction $\text{Me}-\text{C}_6\text{H}_4-\text{I} \xrightarrow{\text{HOH}} [\text{X}]$, [X] will be:



(3) Both (1) and (2)



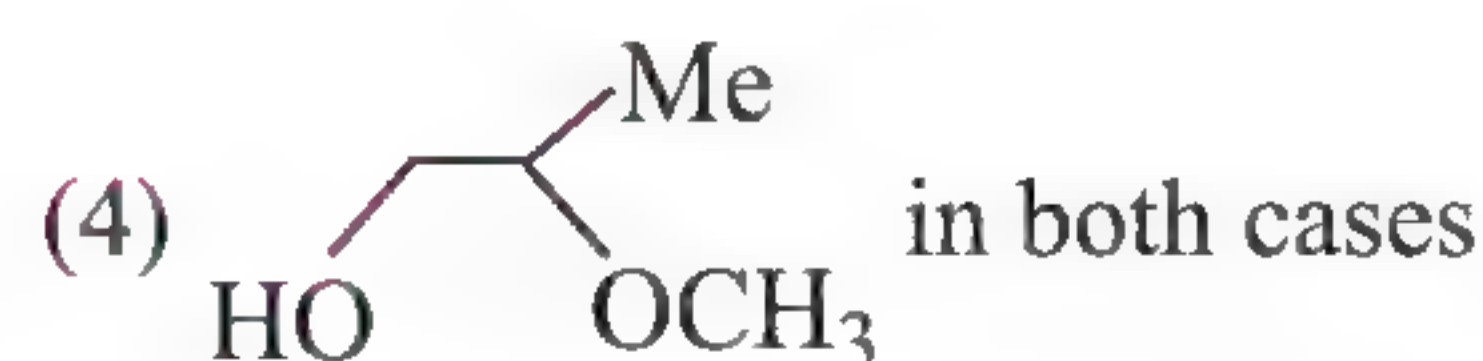
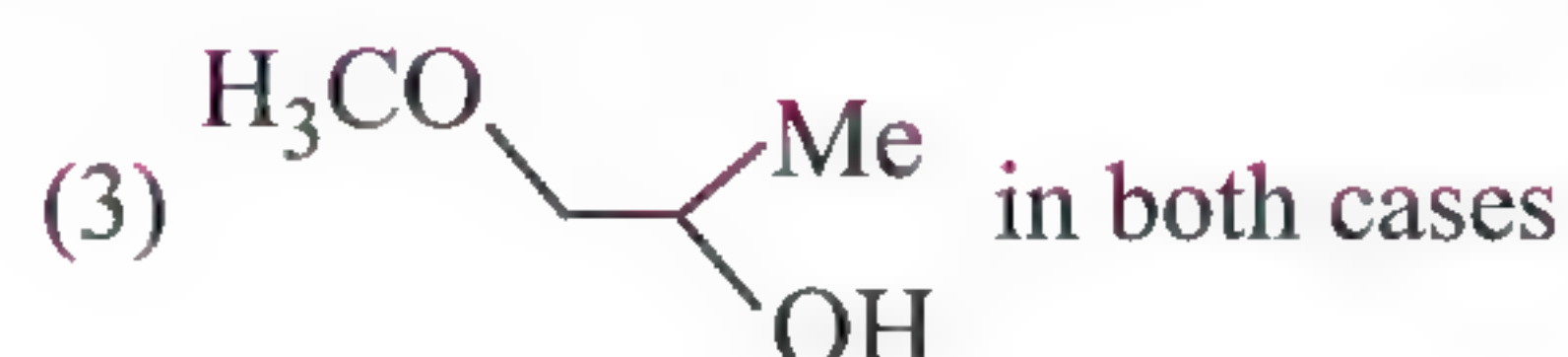
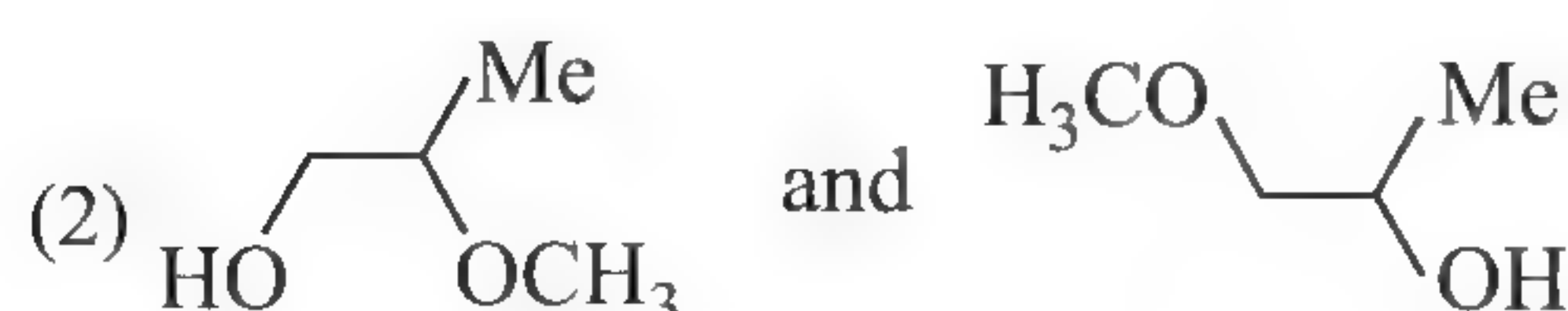
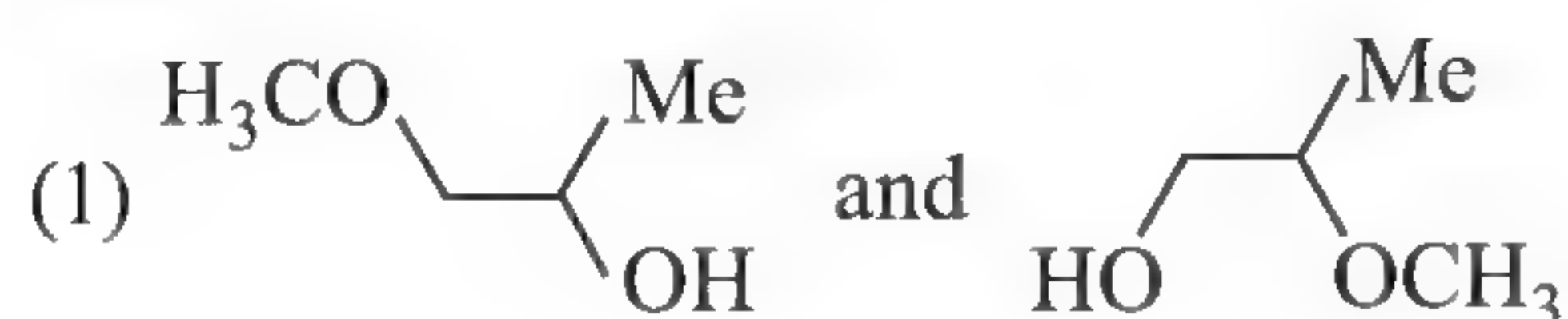
68. In the reaction $\text{Ph}-\text{CH}=\text{CH}-\text{CH}_2\text{Br} \xrightarrow{\text{HOH}} [\text{X}]$, [X] will be:



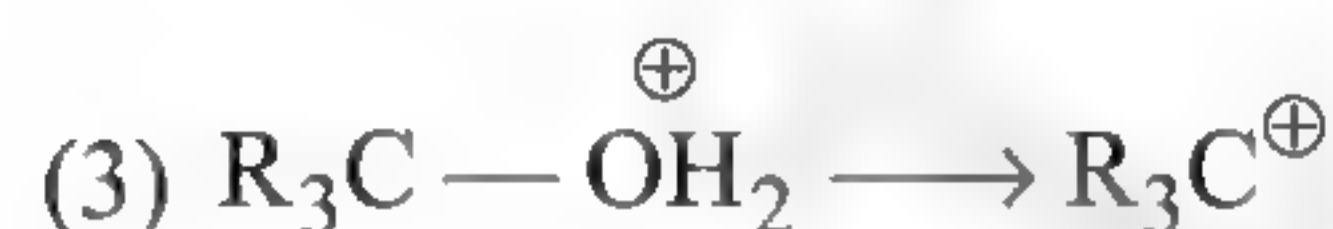
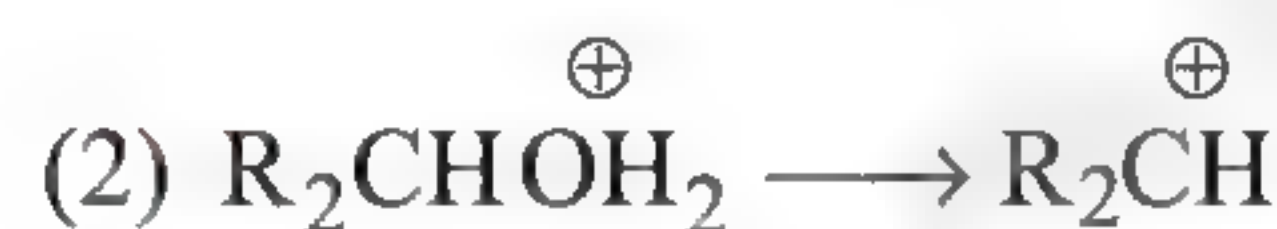
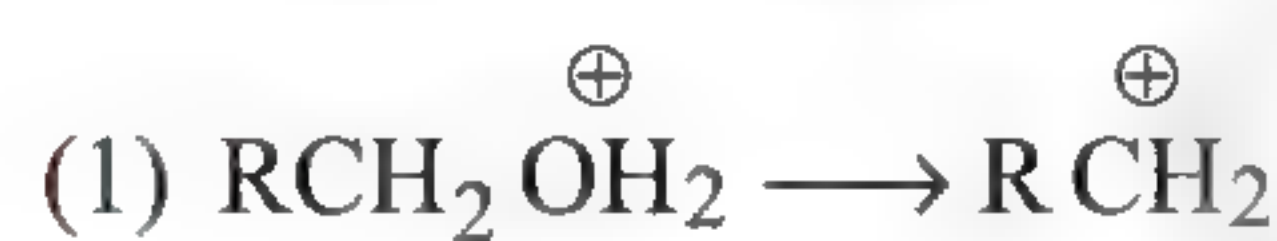
(3) Equimolar mixture of (1) and (2).



69. $[\text{Y}] \xleftarrow[\text{CH}_3\text{ONa}]{\text{CH}_3\text{OH}}$ $\xrightarrow[\text{H}^\oplus]{\text{CH}_3\text{OH}}$ [X], [X] and [Y] are:



70. The energy of activation is lowest for which reaction?



(4) All have the same energy of activation.

71. Choose the incorrect reaction.



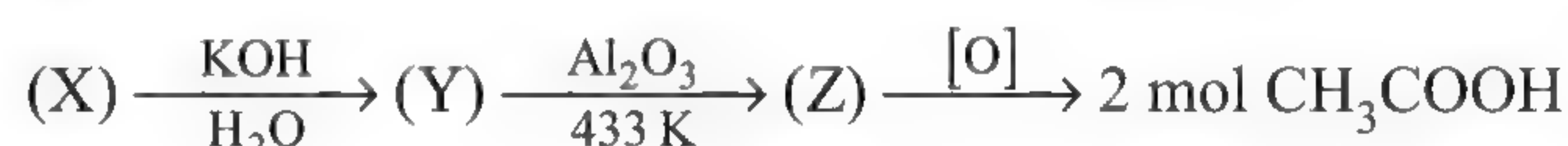
72. Under the influence of air and light, chloroform decomposes into:



73. $\text{C}_6\text{H}_5\text{Cl} \xrightarrow[625 \text{ K and } 300 \text{ atm}]{\text{NaOH (aq.)}} (\text{P})$. The product (P) can be:

(1) Benzal (2) Sodium benzoate
(3) Benzol (4) Sodium phenate

74. In the given sequence of reactions, predict (X).



(1) $\text{CH}_3\text{CH}_2\text{CH}(\text{I})\text{CH}_3$ (2) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{I}$
(3) $\text{CH}_3\text{CH}(\text{I})\text{CH}(\text{I})\text{CH}_3$ (4) $\text{CH}_3\text{CH}(\text{I})\text{CH}_2\text{CH}_2\text{I}$

75. $(\text{CH}_3)_2\text{CHCl} + \text{NaI} \longrightarrow (\text{CH}_3)_2\text{CHI} + \text{NaCl}$

The above reaction is known as:

(1) Perkin's reaction
(2) Finkelstein's reaction
(3) Fitting reaction
(4) Sabatier and Senderan's reaction

76. Which of the following reacting substances will not liberate ethyne gas?

(1) CH_3Cl and Ag (2) CaC_2 and H_2O
(3) CHI_3 and Ag (4) CHCl_3 and Ag

77. Which of the following on reaction with chloroform will give chloretone?

(1) HNO_3 (2) $(\text{CH}_3)_2\text{C}=\text{O}$
(3) Chloral (4) $(\text{CH}_3)_2\text{CHCHO}$

78. Identify (C) in the following series.



- (1) $(\text{CH}_3)_2\text{CH}-\text{CN}$
- (2) $\text{CH}_2=\text{CH}-\text{CH}_2\text{CN}$
- (3) $\text{Br}-\text{CH}=\text{CH}-\text{CN}$
- (4) $\text{CH}_2=\text{CH}-\underset{\text{Br}}{\text{CHCN}}$

79. Which of the following halides has the least dipole moment?

- (1) 1,2-Dichlorobenzene
- (2) Dichloromethane
- (3) Trichloromethane
- (4) Ethyl chloride

80. An ethereal solution of 4-nitrochlorobenzene is treated with metallic sodium. The product formed is:

- (1) Aminobenzene
- (2) 4,4-Dinitrodiphenyl
- (3) *p*-Chloroaniline
- (4) Benzene diazonium chloride

81. A halide with formula $\text{C}_6\text{H}_{13}\text{Br}$ gave two isomeric alkenes (A) and (B) with formula C_6H_{12} . On reductive ozonolysis of a mixture of (A) and (B), the following compounds were obtained: CH_3COCH_3 , CH_3CHO , $\text{CH}_3\text{CH}_2\text{CHO}$, and $(\text{CH}_3)_2\text{CHCHO}$. The halide is:

- (1) 2-Bromohexane
- (2) 3-Bromo-2-methylpentane
- (3) 2,2-Dimethyl-1-bromohexane
- (4) Unpredictable

82. Vinyl chloride and ethyl chloride can be distinguished by:

- (1) Lucas reagent
- (2) KOH , AgNO_3
- (3) AgCl
- (4) HCl/AgCl

83. The most reactive compound for electrophilic nitration will be:

- (1) Toluene
- (2) Benzoic acid
- (3) Nitrobenzene
- (4) Benzene

84. Slow oxidation of chloroform in air leads to the formation of:

- (1) Formyl chloride
- (2) Formic acid
- (3) COCl_2
- (4) Trichloro acetic acid

85. Which of the following is most easily cleaved by HBr ?



86. Which will react faster with NBS?

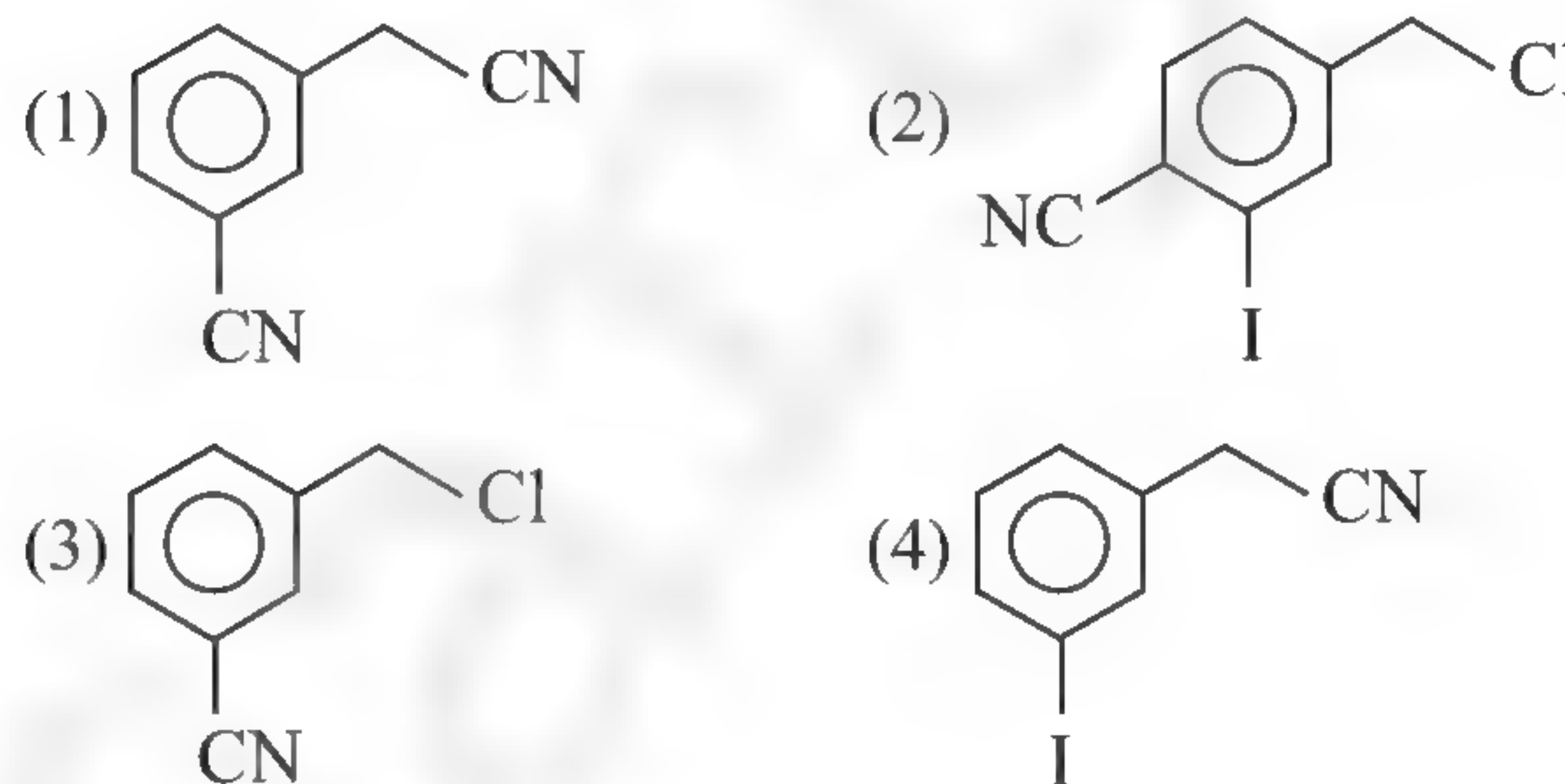
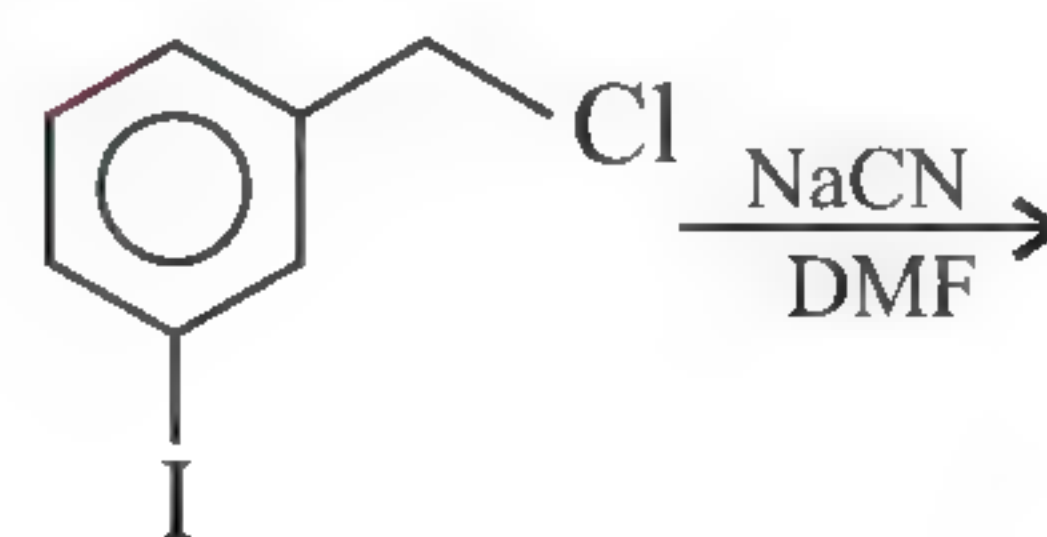
- (1) C_6H_6
- (2) CH_4
- (3) Toluene
- (4) Cyclopropane

87. Which of the following on reaction with acetylene ($\text{CH}\equiv\text{CH}$) produce gas(es)?

- I. K in liquid NH_3
- II. NH_2^\ominus
- III. CH_3^\ominus
- IV. OH^\ominus

- (1) (I), (II), and (III)
- (2) (I), (II), and (IV)
- (3) (II), (III), and (IV)
- (4) (I), (III), and (IV)

88. The structure of the major product formed in the following reaction is:



89. $\text{CH}_3-\text{Br} + \text{Nu}^\ominus \longrightarrow \text{CH}_3-\text{Nu} + \text{Br}^\ominus$

The decreasing order of the rate of the above reaction with nucleophile (Nu^\ominus) (A) to (D) is:

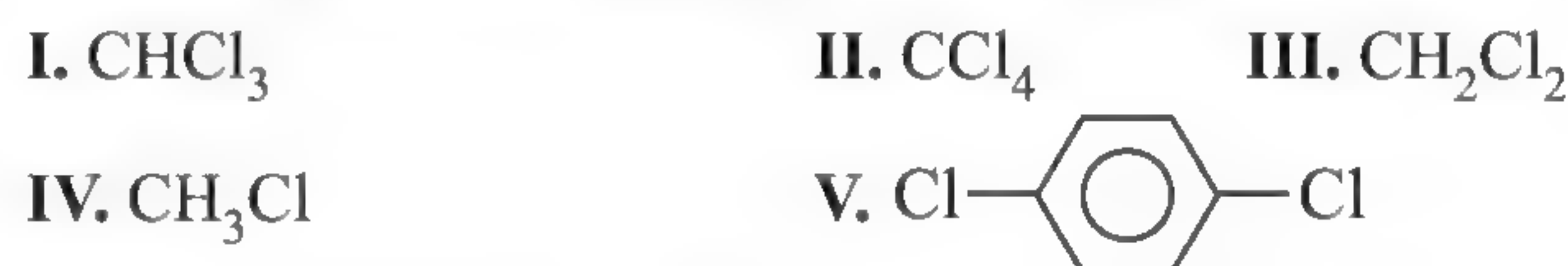


- (1) (D) > (C) > (A) > (B)
- (2) (D) > (C) > (B) > (A)
- (3) (C) > (D) > (A) > (B)
- (4) (B) > (D) > (C) > (A)

90. HBr reacts with $\text{CH}_2=\text{CH}-\text{OCH}_3$ under anhydrous conditions at room temperature to give:

- (1) CH_3CHO and CH_3Br
- (2) BrCH_2CHO and CH_3OH
- (3) $\text{BrCH}_2\text{CH}_2\text{OCH}_3$
- (4) $\text{CH}_3-\text{CH}(\text{Br})-\text{OCH}_3$

91. Consider the following halogen-containing compounds:



The compounds with a net zero dipole moment are:

- (1) (II), (V)
- (2) (II)
- (3) (III), (IV)
- (4) (I), (IV)

92. Which of the following has the highest boiling point?

- (1) $\text{C}_3\text{H}_7\text{Cl}$
- (2) $\text{C}_4\text{H}_9\text{Cl}$
- (3) $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{Cl}$
- (4) $(\text{CH}_3)_3\text{C}-\text{Cl}$

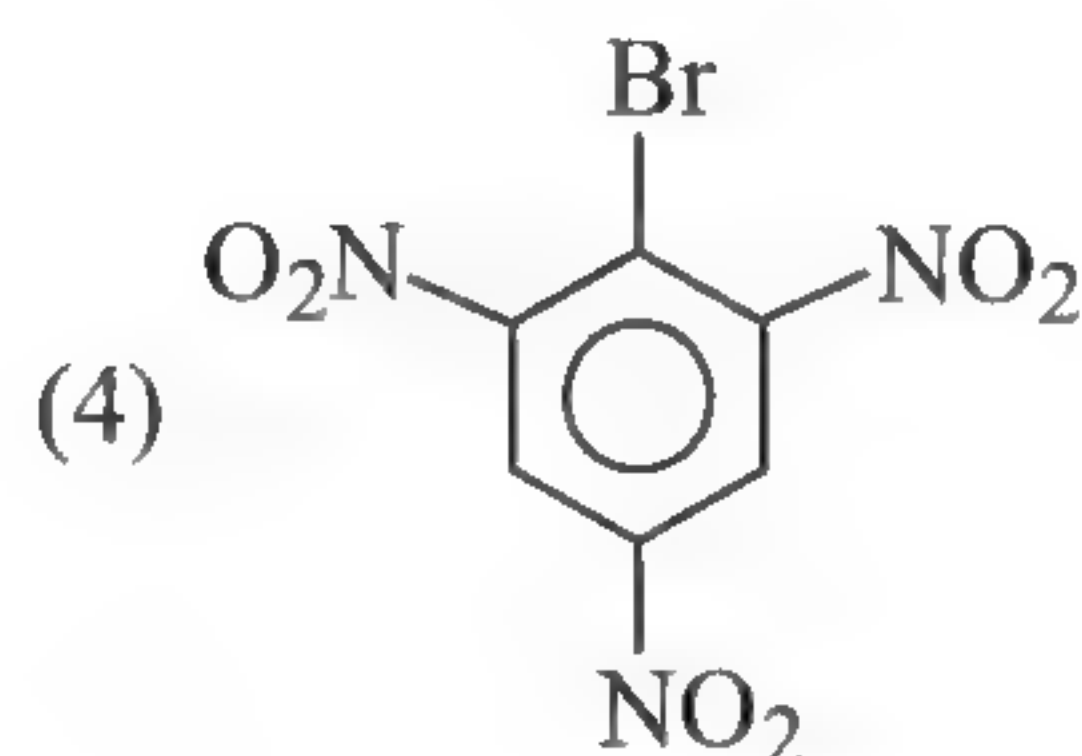
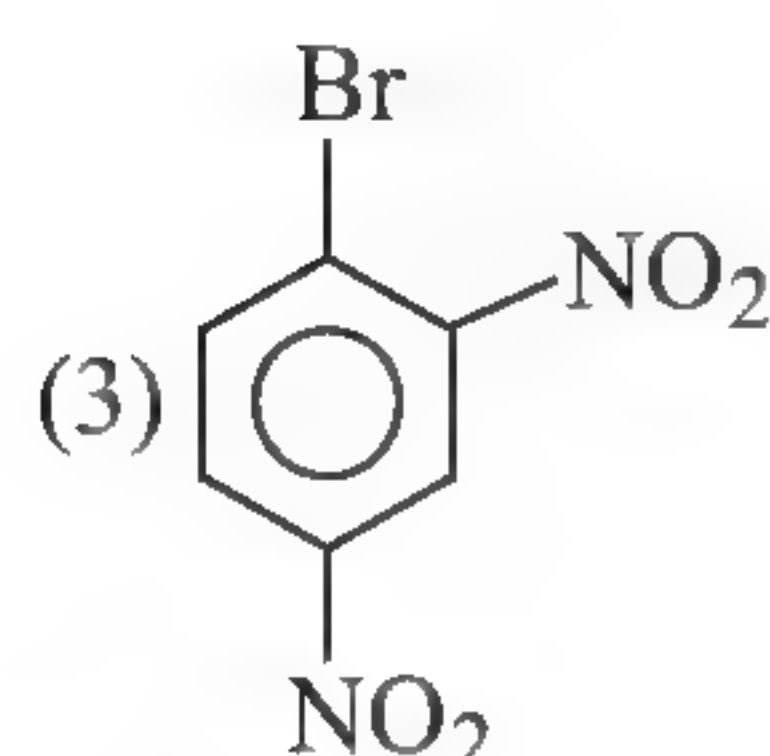
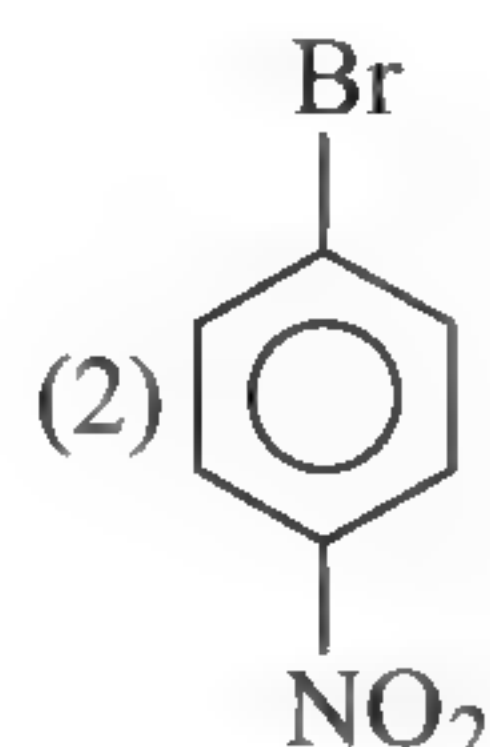
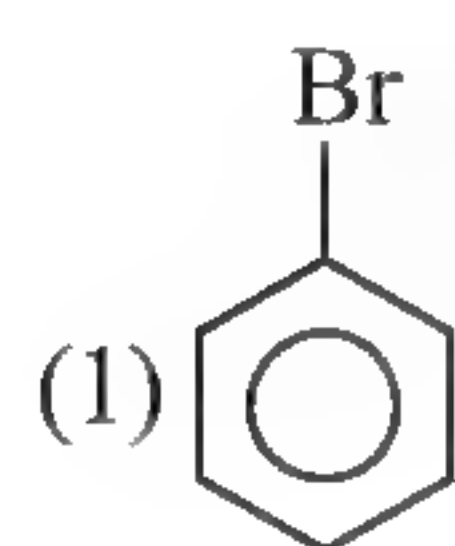
93. Which of the following sequence of reactions (reagents) can be used for the conversion of PhCH_2CH_3 into $\text{PhCH}=\text{CH}_2$?

- (1) SOCl_2 ; H_2O
- (2) SO_2Cl_2 ; alc. KOH
- (3) $\text{Cl}_2/h\nu$; H_2O
- (4) SOCl_2 ; alc. KOH

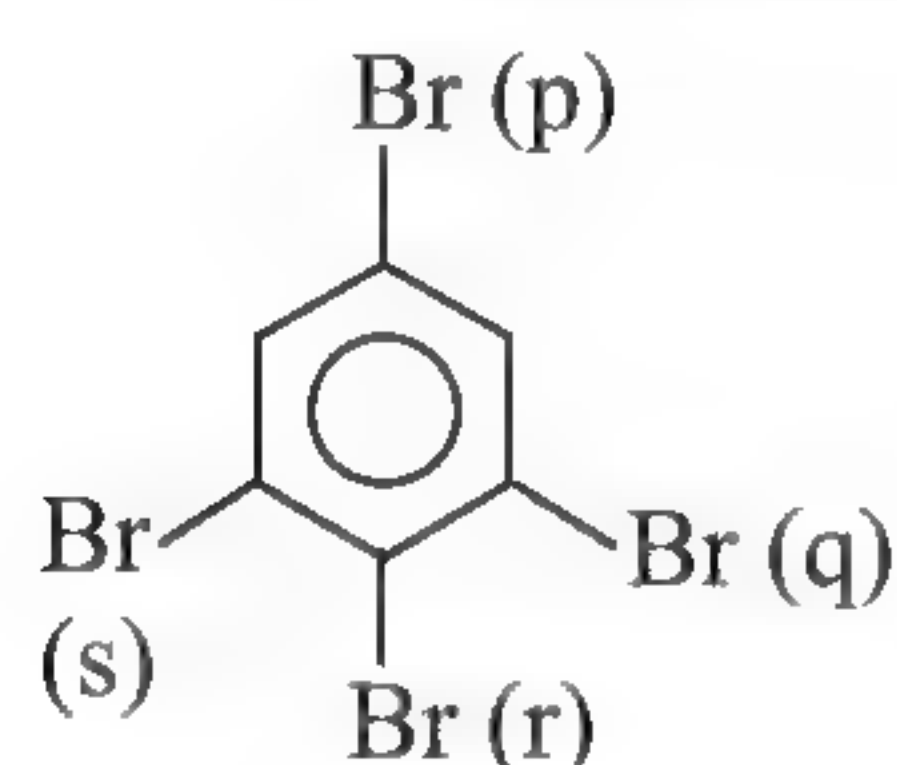
94. The decreasing order of dipole moment of the following is:

- I. CH_3Cl
- II. CH_3Br
- III. CH_3F
- (1) (I) > (II) > (III)
- (2) (I) > (III) > (II)
- (3) (II) > (I) > (III)
- (4) (II) > (III) > (I)

95. Red colour precipitate is obtained when which of the following compounds reacts with KOH?

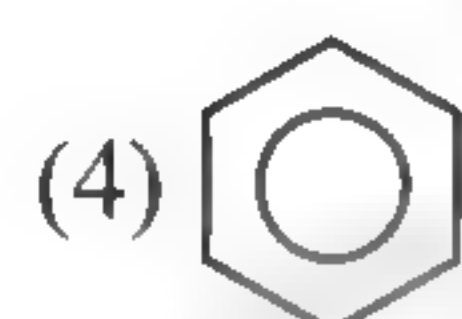
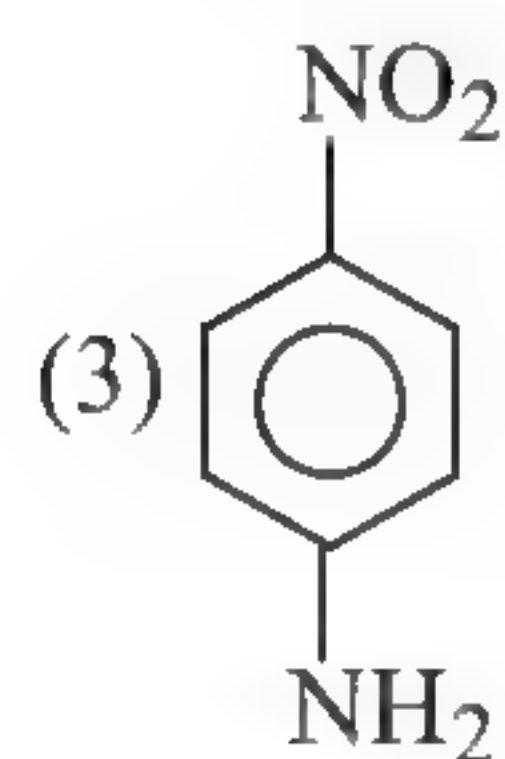
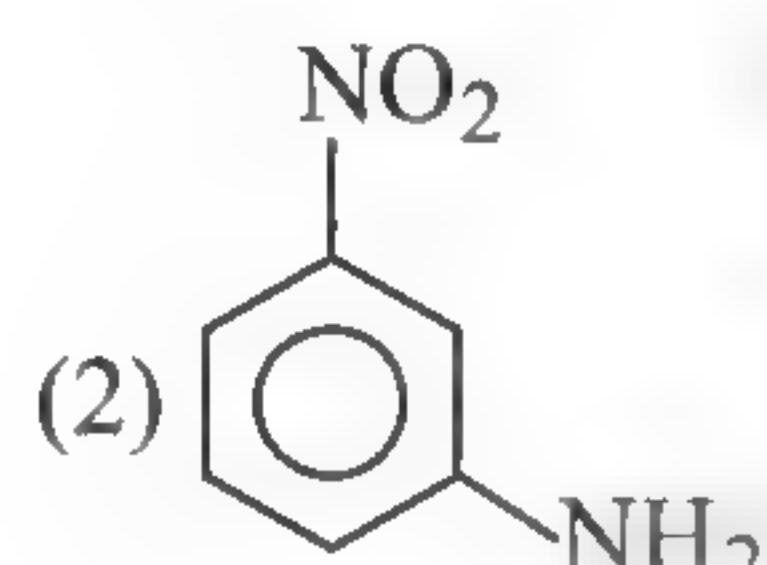
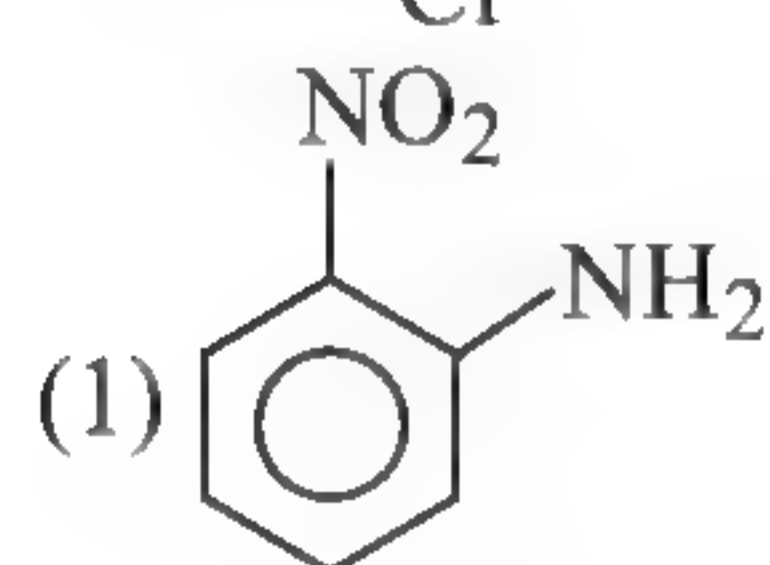
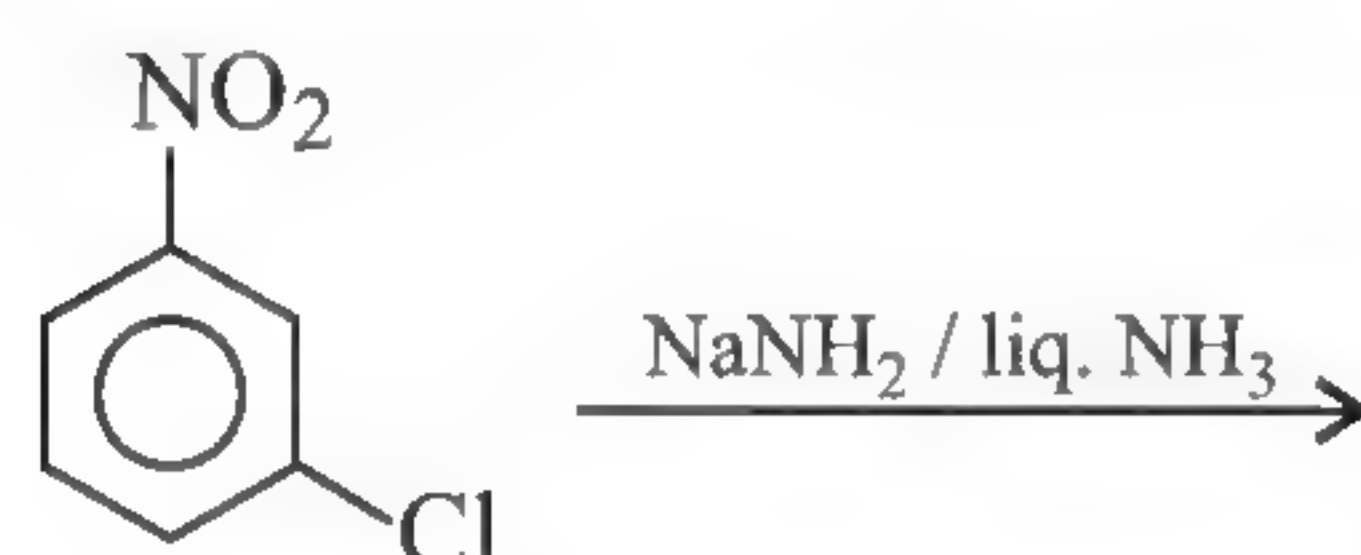


96. Which 'Br' is first substituted on reaction with NaOH?

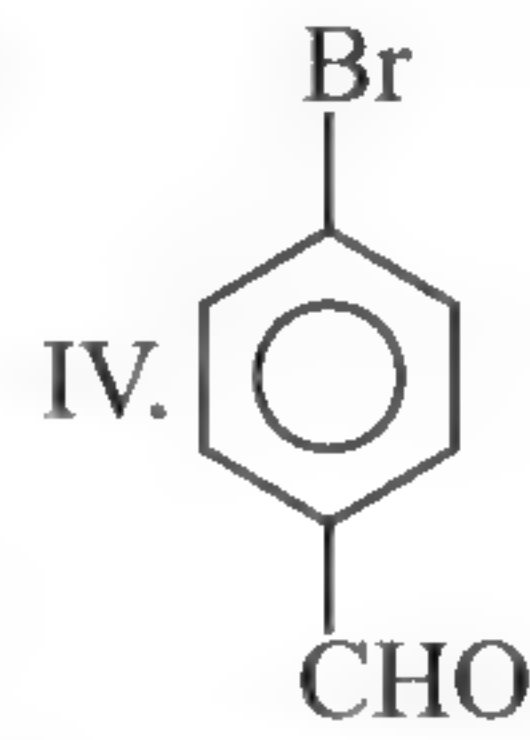
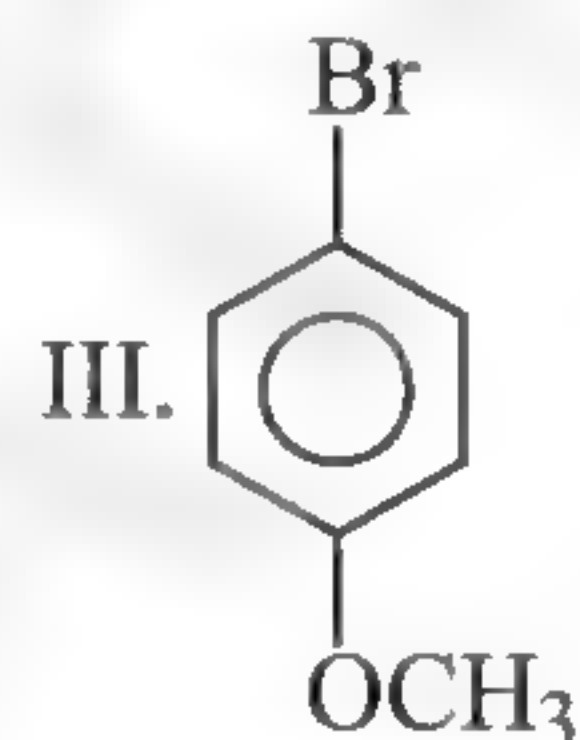
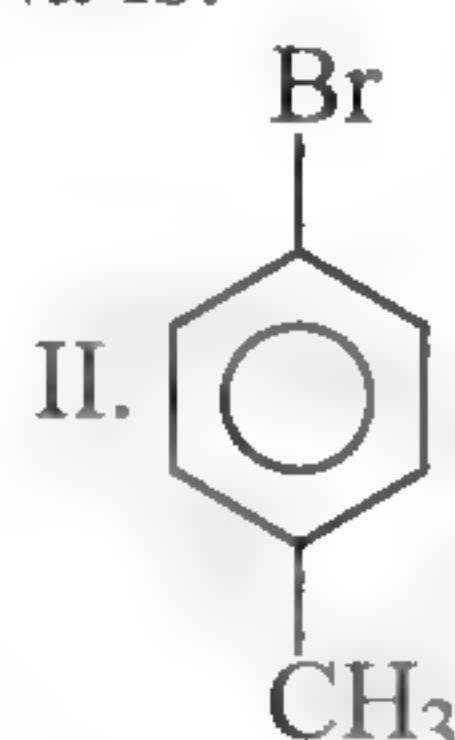
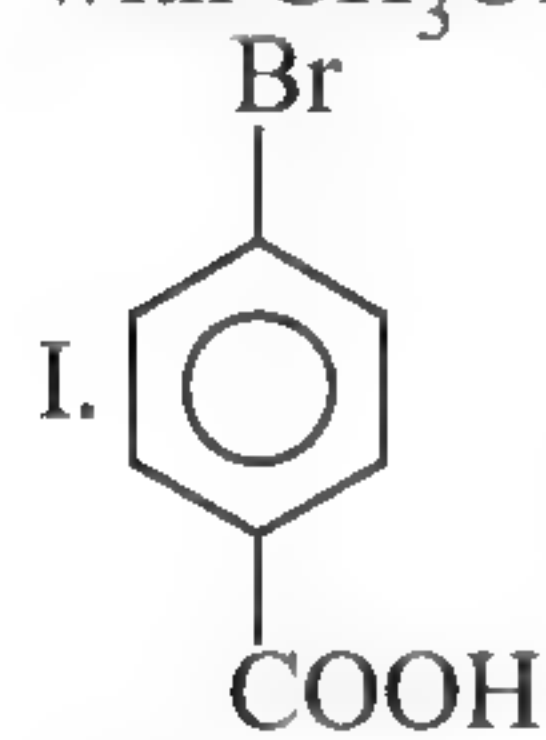


- (1) p (2) q
(3) r (4) s

97. The major product obtained in the following reaction is:

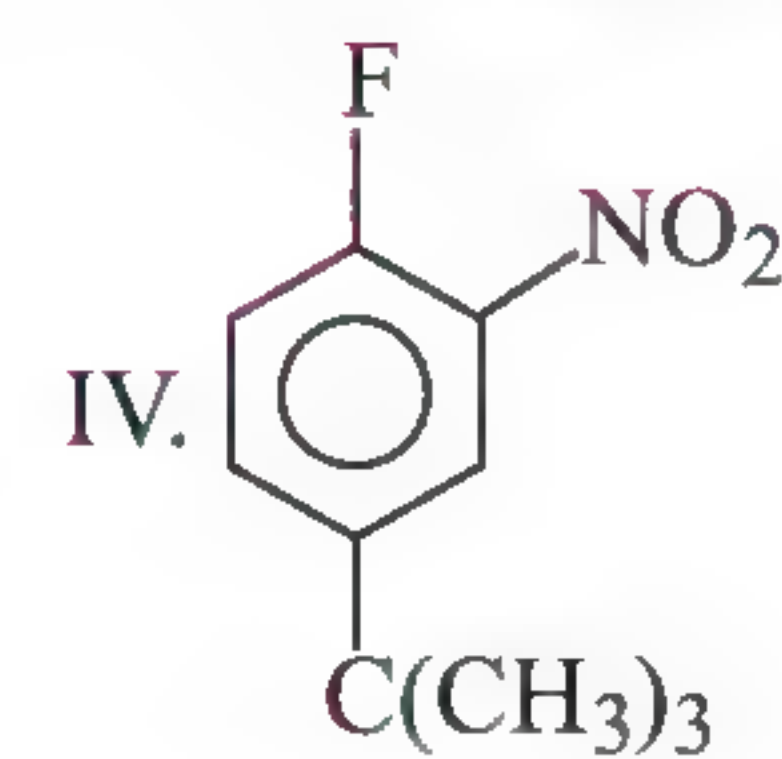
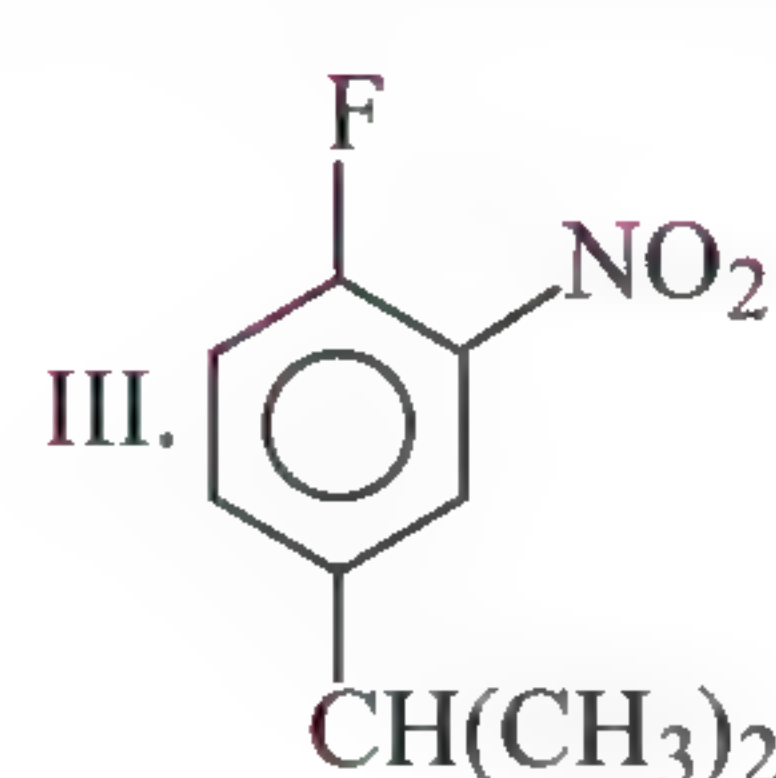
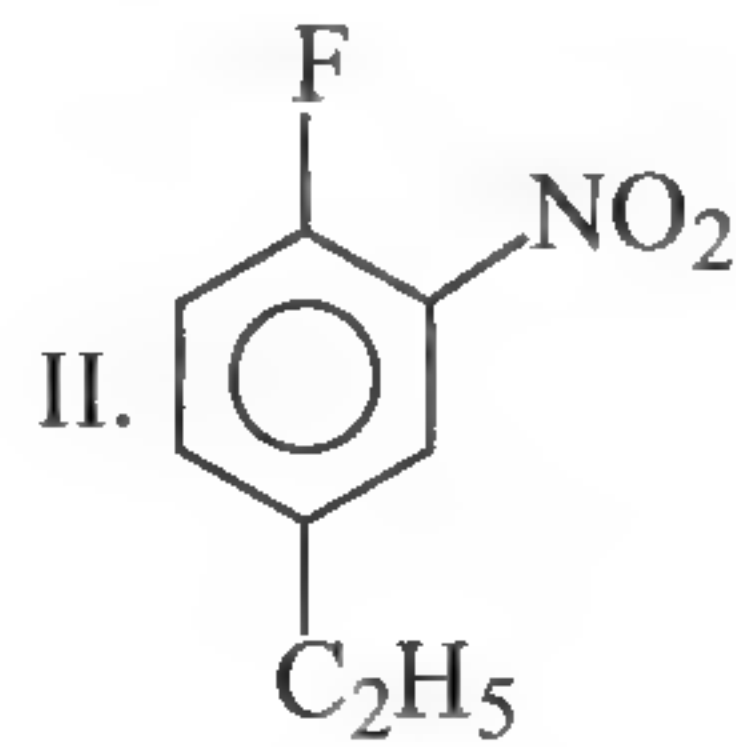
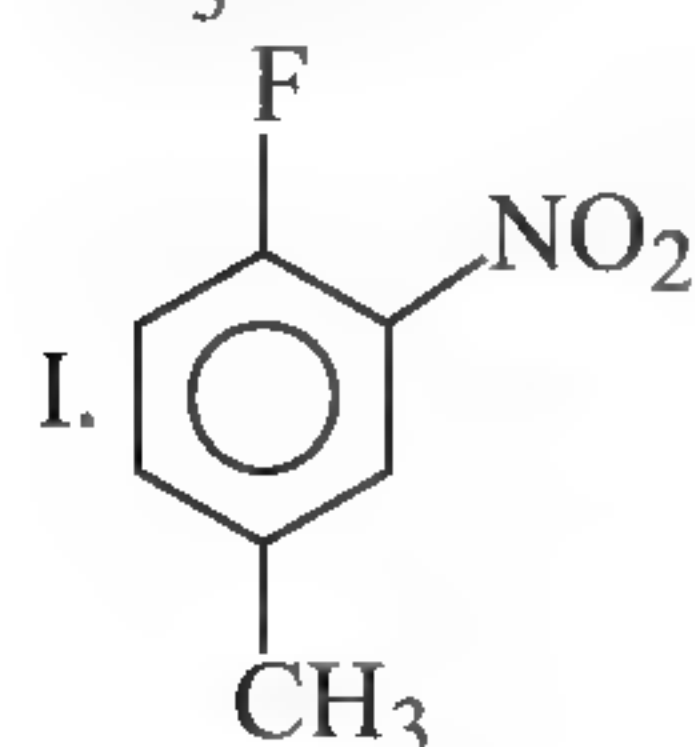


98. Decreasing order of the ArSN reaction of the following with CH_3ONa is:



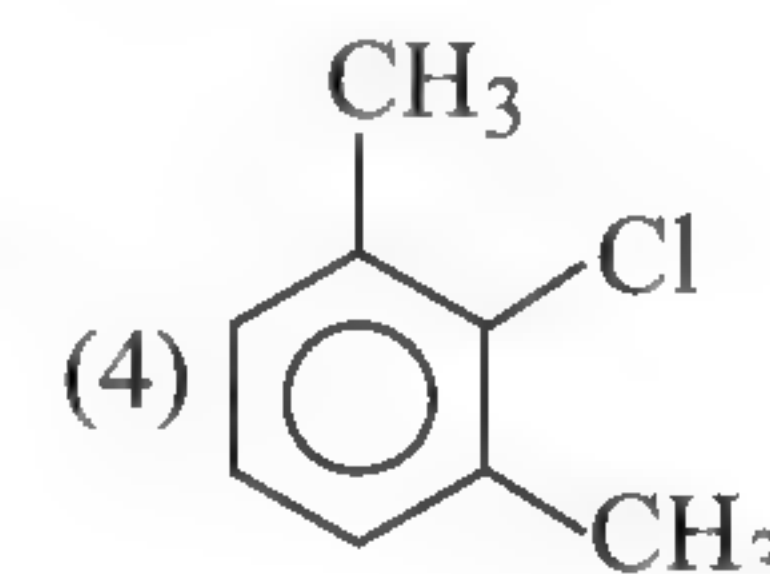
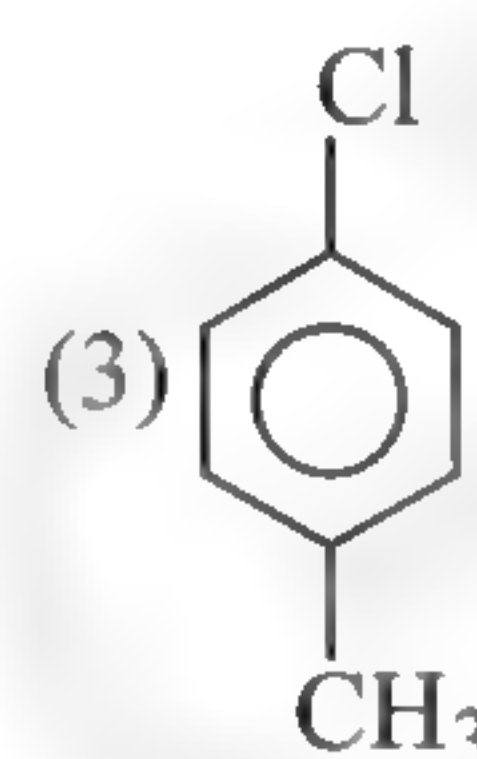
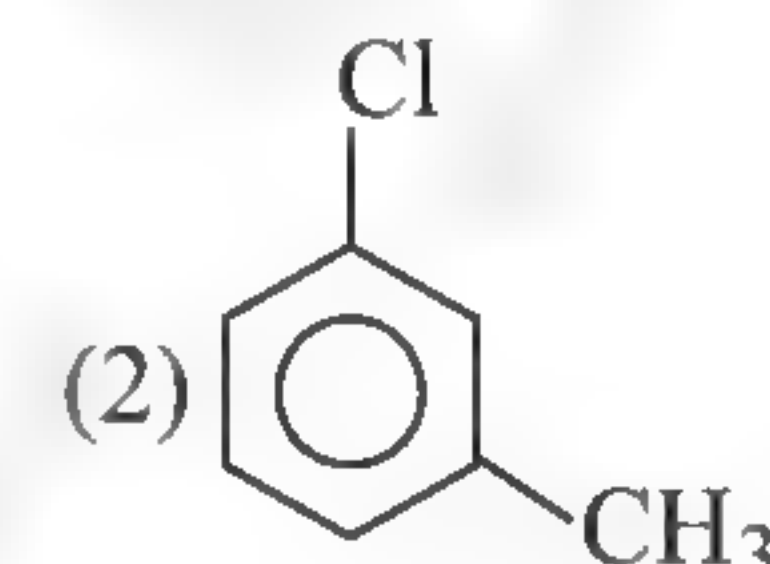
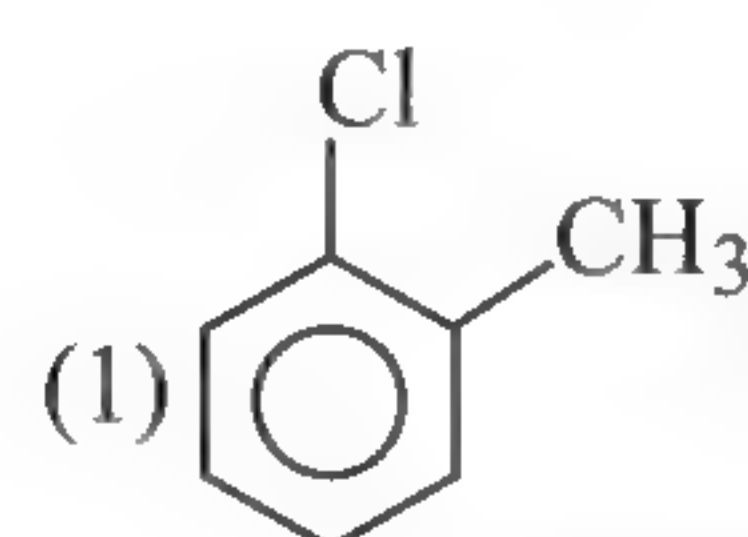
- (1) IV > I > II > III (2) IV > I > III > II
(3) III > II > I > IV (4) II > III > I > IV

99. Decreasing order of ArSN reaction of the following with CH_3OK is:

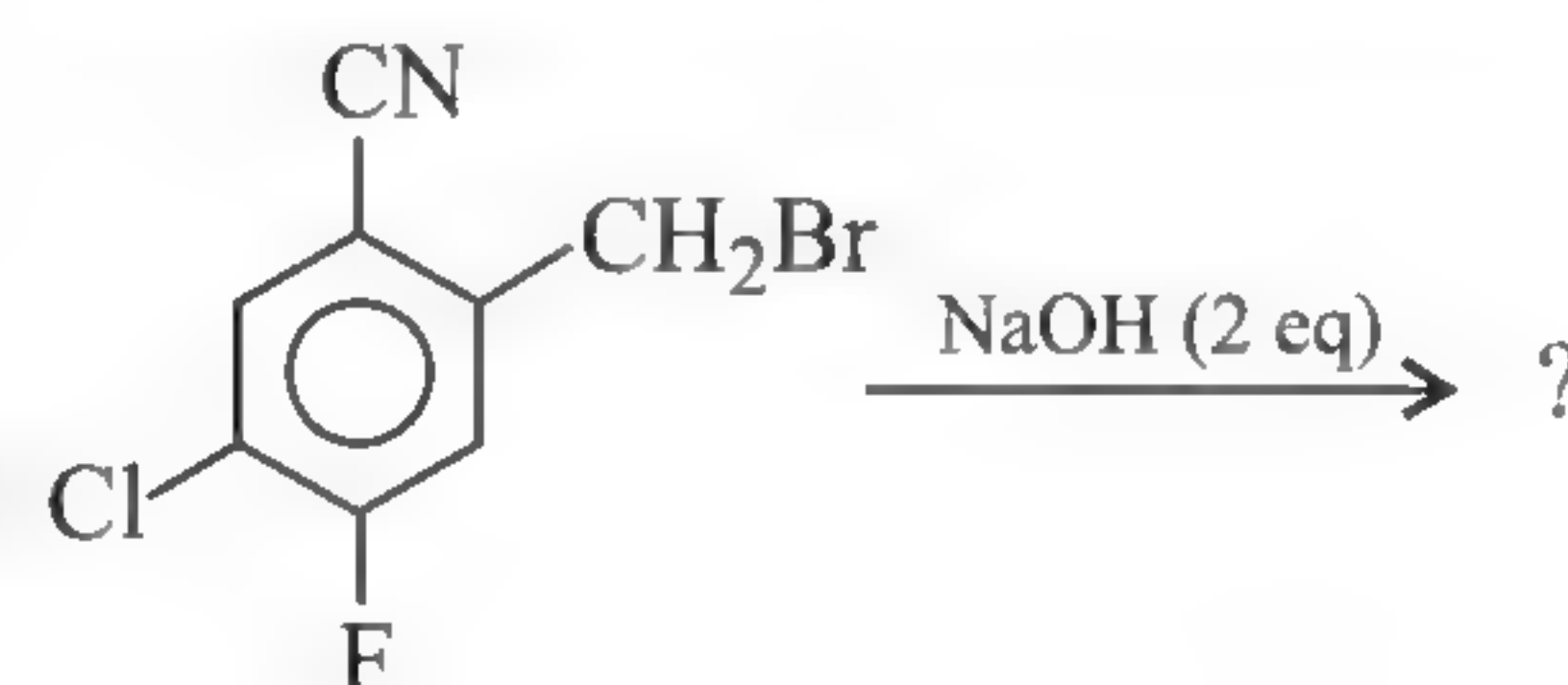


- (1) I > II > III > IV (2) IV > III > II > I
(3) IV > I > II > III (4) III > II > I > IV

100. Which compound on reaction with $\text{NaNH}_2/\text{liq NH}_3$ gives all types of *o*-, *m*- and *p*-substituted product?



101. Which halogen atom/group is present in the final major product of the following reaction?



- (1) F (2) Cl
(3) Br (4) CN

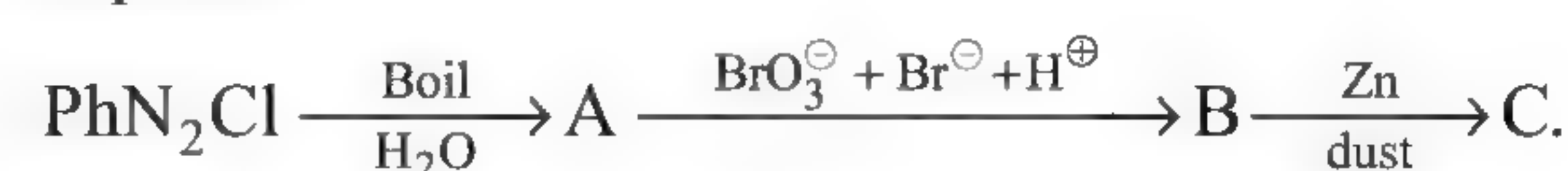
102. Select the correct statement.

- (1) CCl_4 is obtained by reaction of CS_2 and Cl_2 in presence of AlCl_3
(2) S_2Cl_2 is called pyrene.
(3) Toxic phosgene formed in the CHCl_3 bottles are removed by adding methanol to it.
(4) CHCl_3 on reaction of silver powder gives ethene.

103. Which of the following reactions represents Borodine-Hunsdieker reaction?

- (1) $\text{Ethylchloride} + \text{CoF}_3 \longrightarrow \text{Ethyl fluoride} + \text{CoCl}_2$
(2) $(\text{Ph CH}_2 \text{ COO})_2 \text{Pb} + \text{Br}_2/\text{CCl}_4 \longrightarrow \text{Ph CH}_2 \text{ Br} + \text{CO}_2 + \text{PbBr}_2$
(3) $2\text{CH}_3 \text{ CH}_2 \text{ COO Ag} + \text{I}_2 \longrightarrow \text{CH}_3 \text{ CH}_2 \text{ COO CH}_2 \text{ CH}_3 + \text{CO}_2 + 2\text{Ag I}$
(4) $\text{C}_2 \text{H}_5 \text{ Br} + \text{Na I} \longrightarrow \text{C}_2 \text{H}_5 \text{ I} + \text{NaBr}$

104. Select the in correct statement about the following reaction sequence.



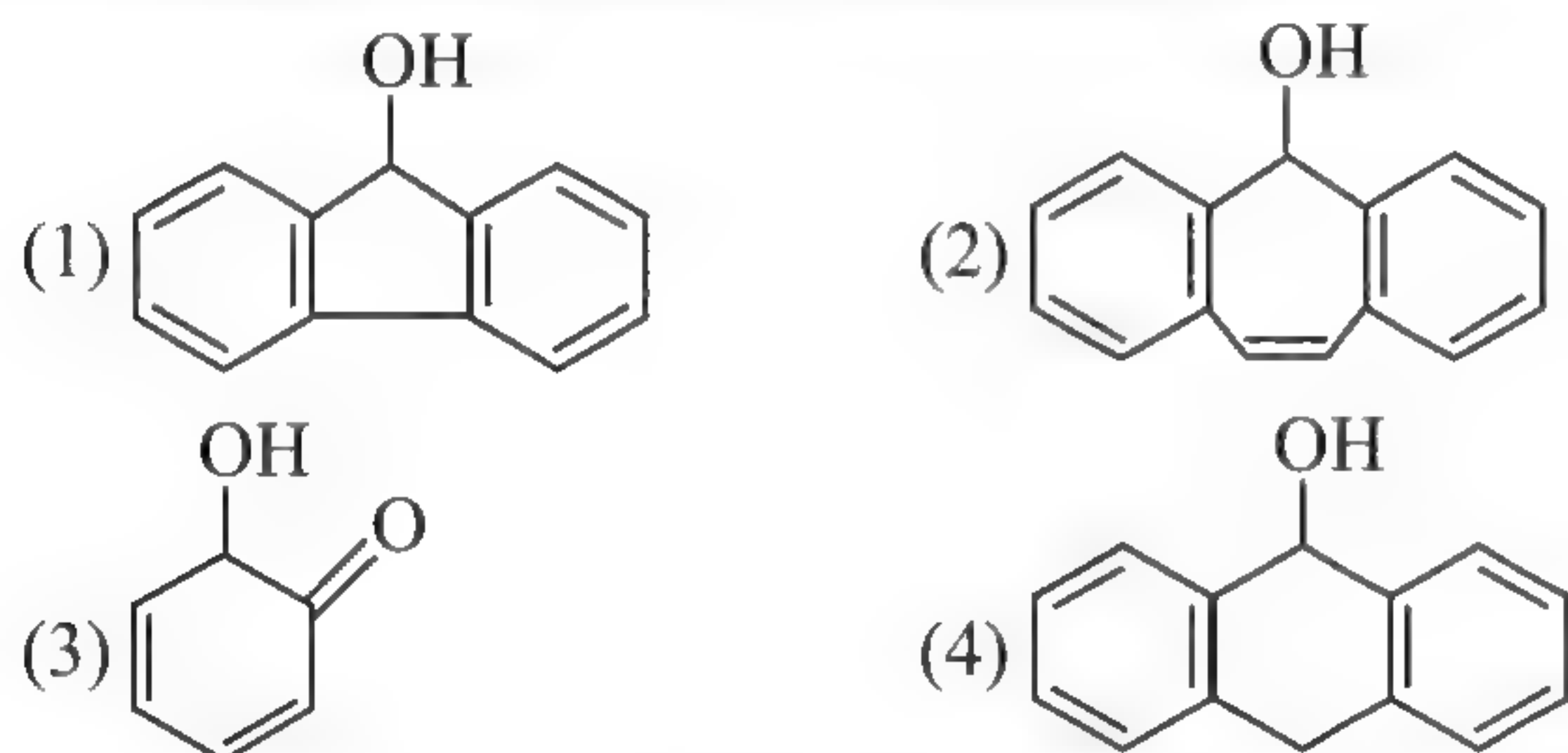
- (1) Product B is 2, 3, 5-tribromo phenol.
(2) Product C is symmetrical tribromo benzene.
(3) Dipole moment of product C is zero.
(4) Dipole moment of product B is less than product C.

105. Which of the following statements is correct?

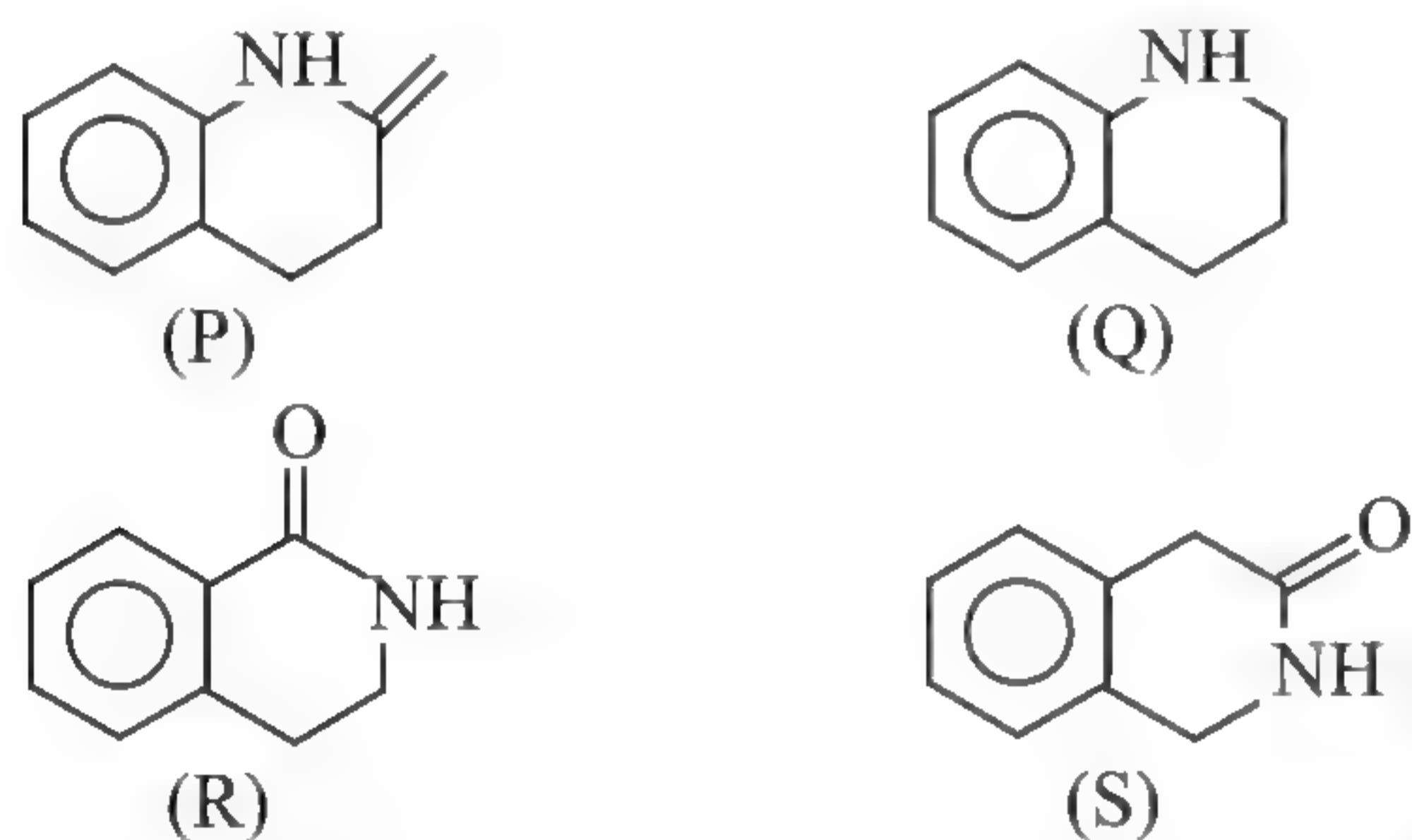
- (1) Ethanenitrile is hydrolysed by both in acidic or alkaline medium to give propanoic acid.
- (2) Ethyl isocyanide on partial hydrolysis in acidic medium gives ethyl amine and methanoic acid.
- (3) In the hydrolysis of carbylamine, electrophile and nucleophile add to the same C-atom.
- (4) Ethyl bromide on reaction with potassium nitrite give nitro ethane as the major product.

Miscellaneous

106. Which of the following alcohol would you expect to form a carbocation most readily in sulphuric acid ?

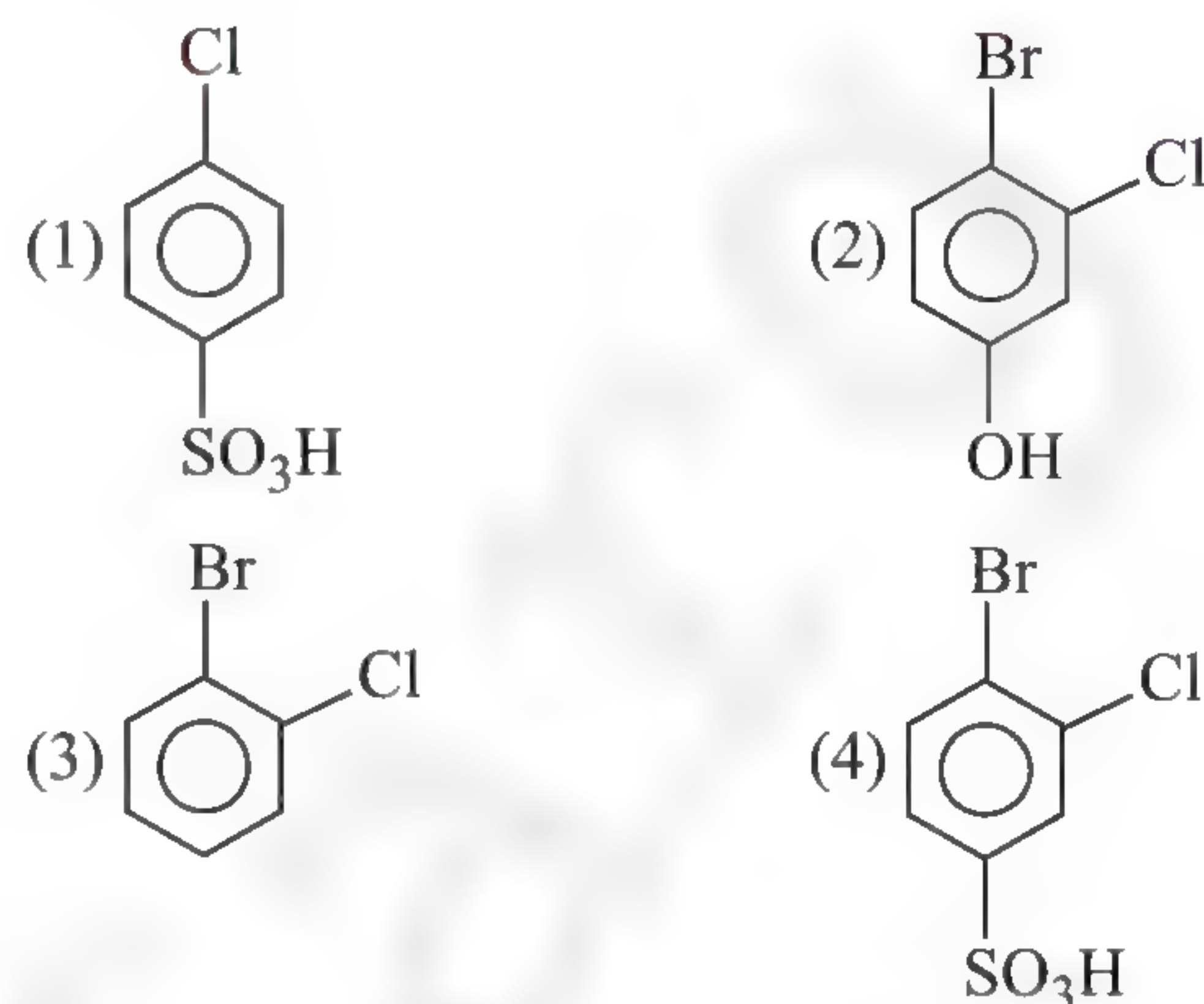
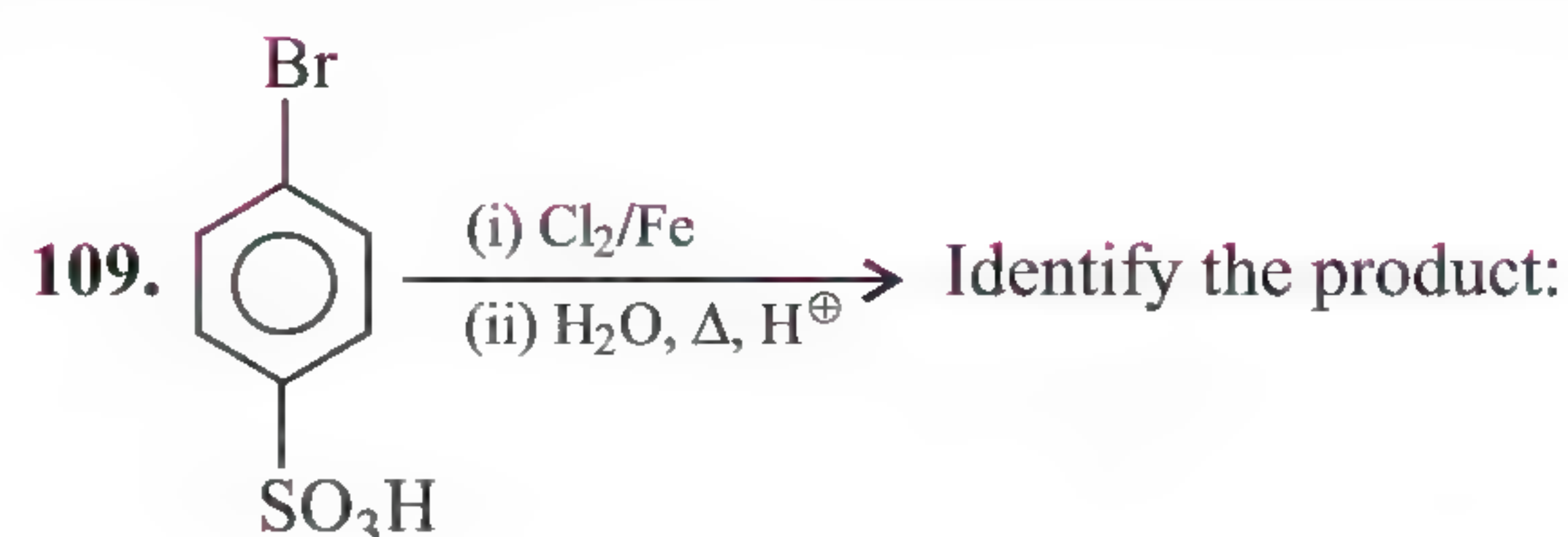
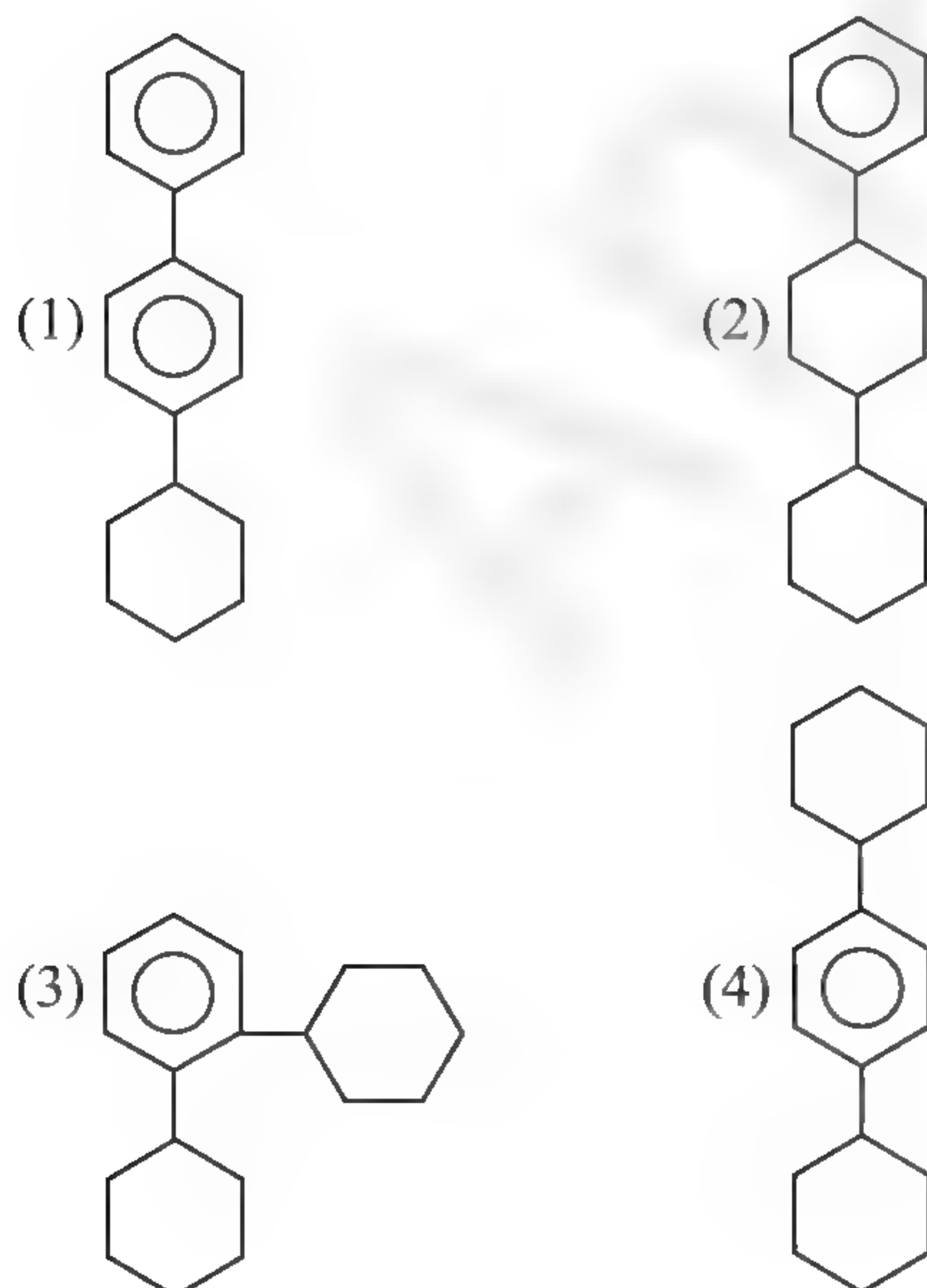
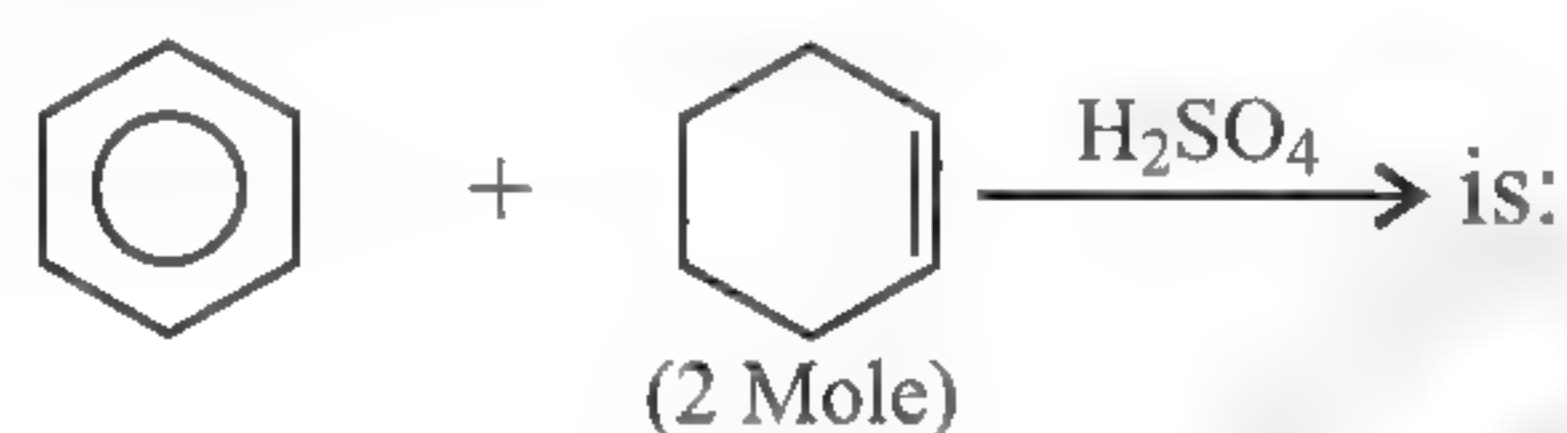


107. Order of rate of electrophilic substitution reaction is:

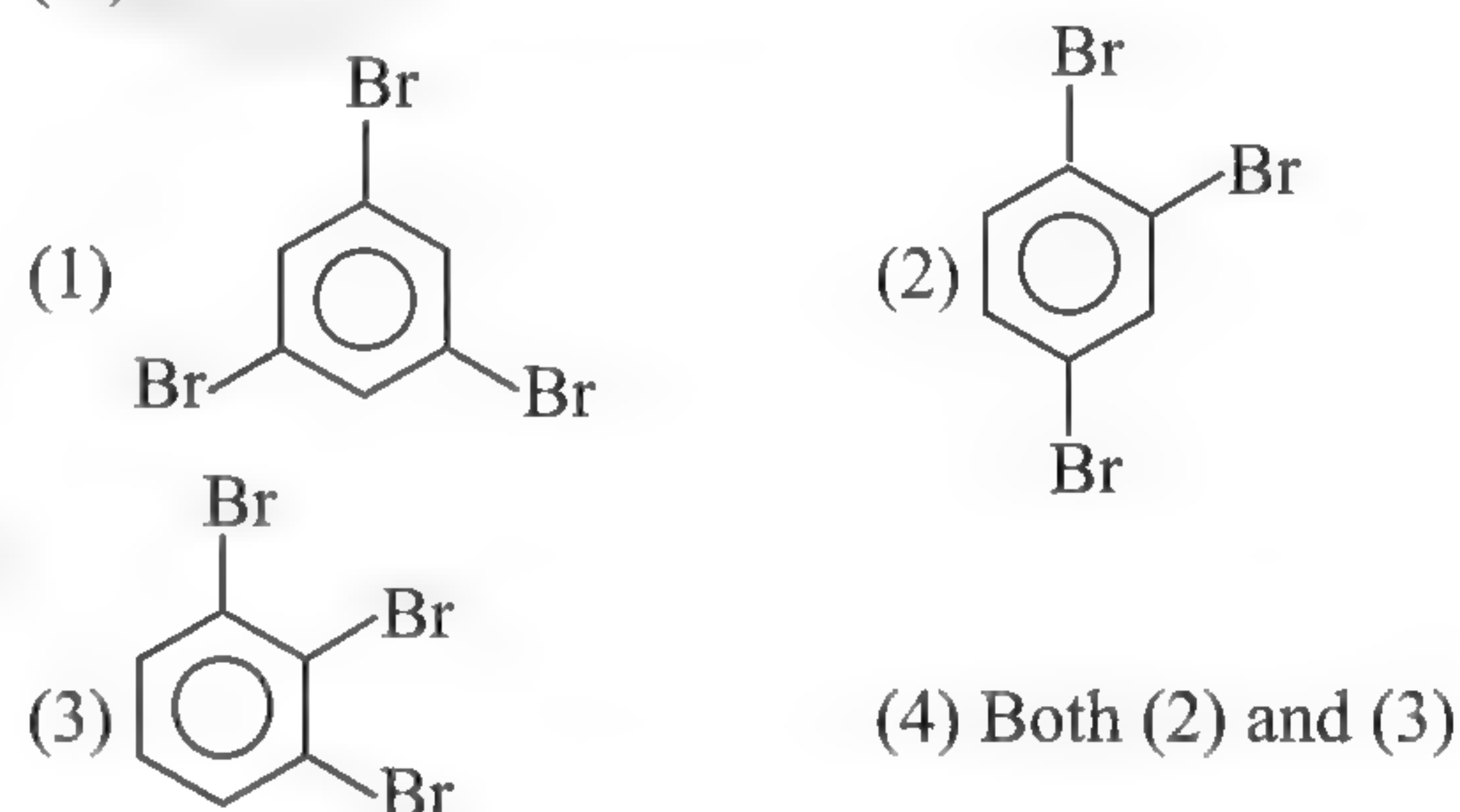


- (1) $Q > P > S > R$
- (2) $Q > P > R > S$
- (3) $P > Q > S > R$
- (4) $P > Q > R > S$

108. Major product obtained in the given reaction

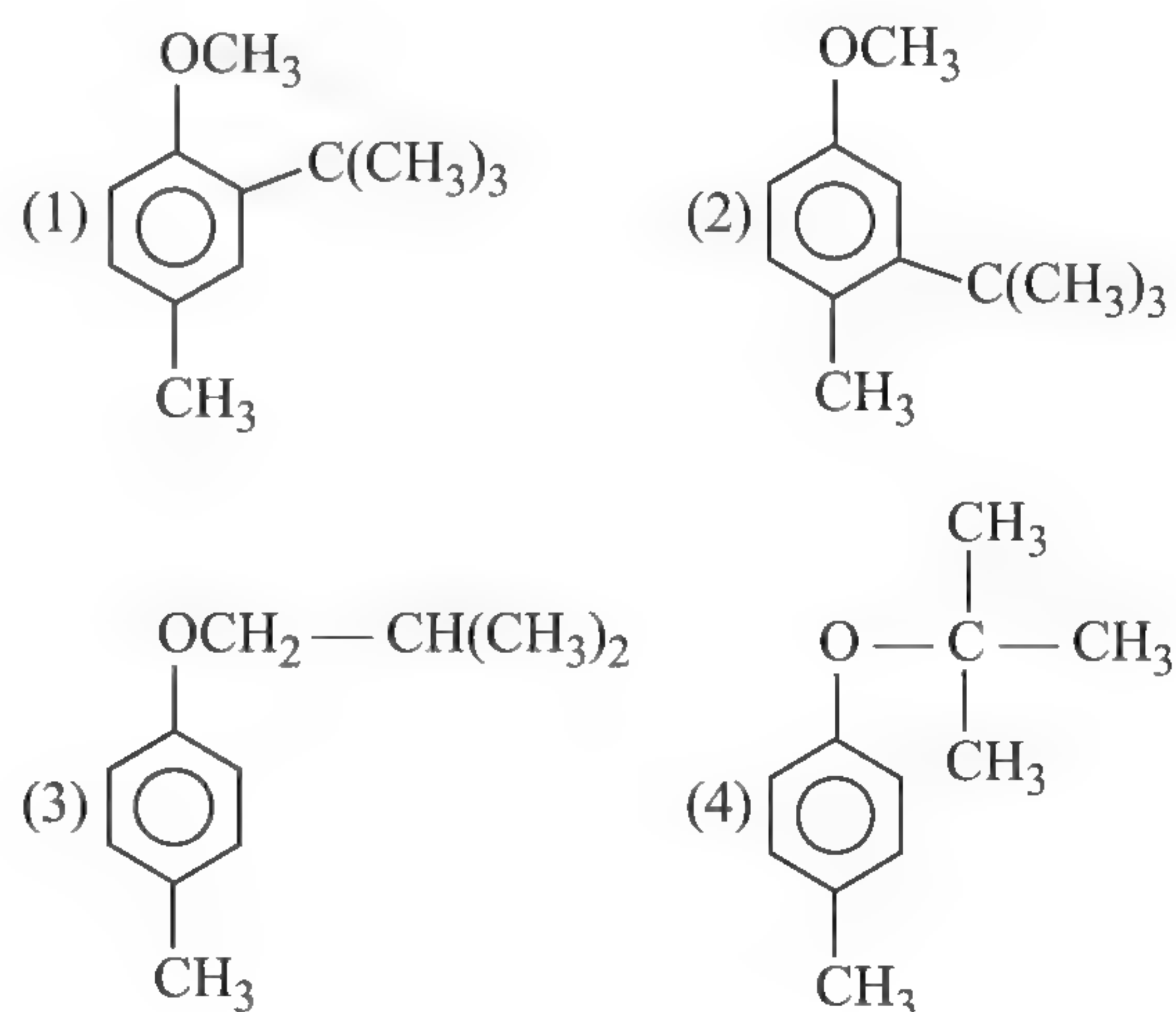
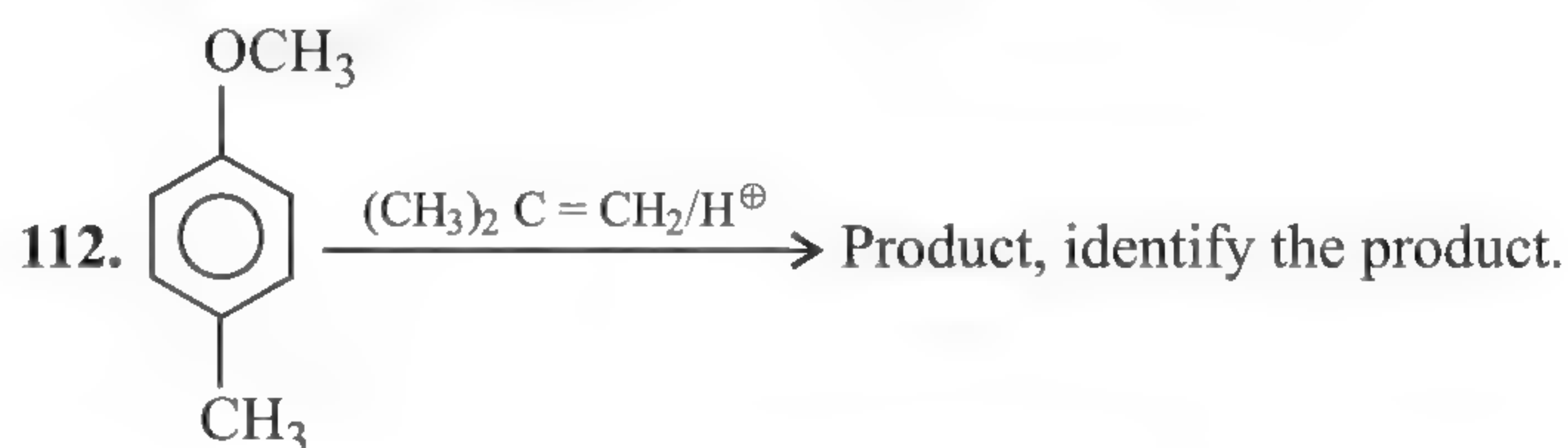


110. A particular form of Tribromobenzene (X) forms three mononitrotribromobenzene. The structure of the compound (X) is:

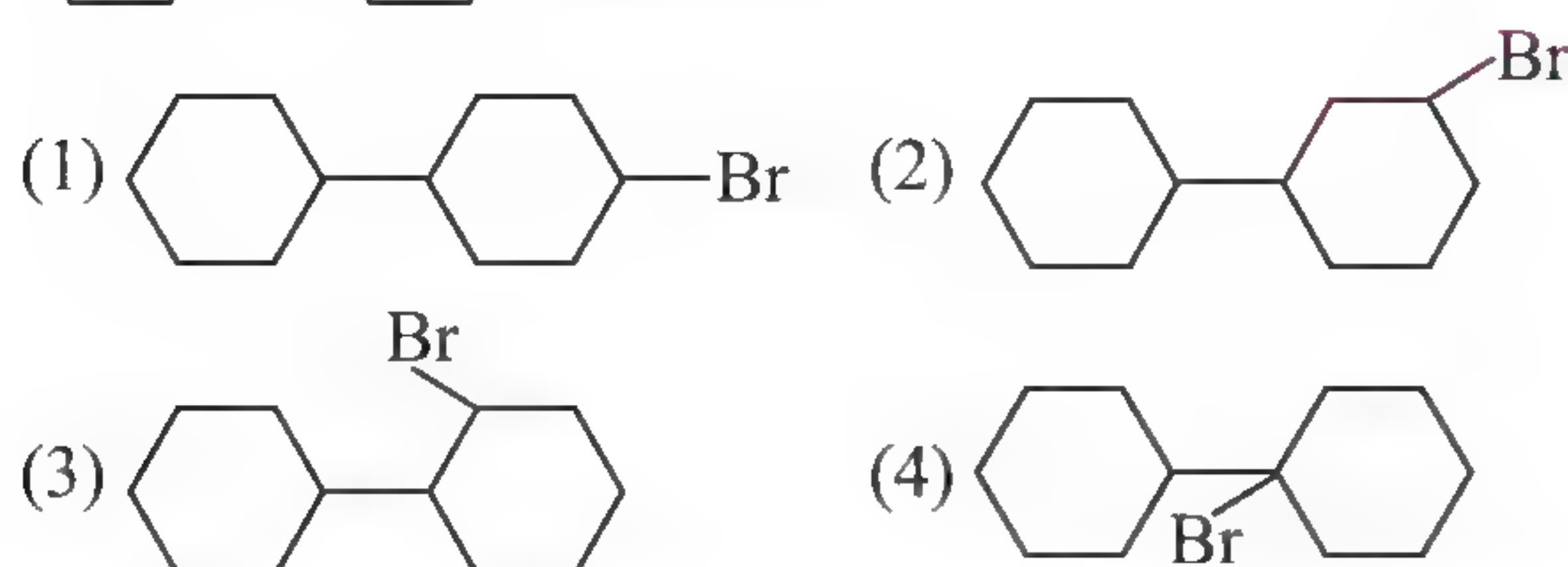
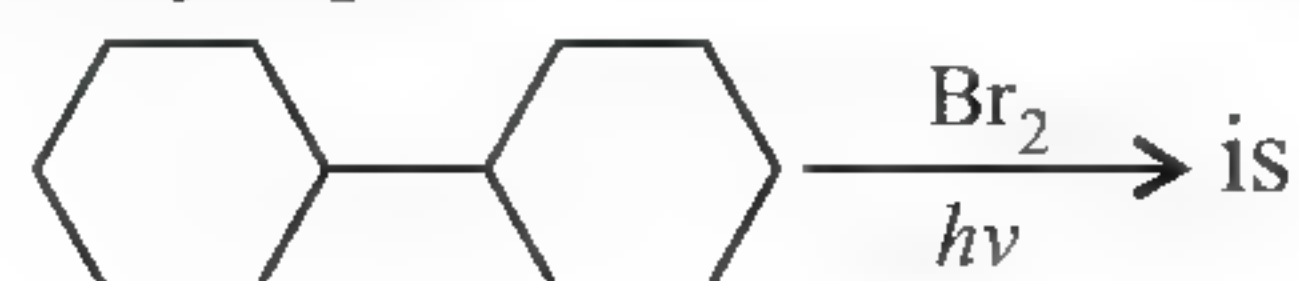


111. The reaction of benzene with CO and HCl in the presence of anhydrous AlCl_3 gives

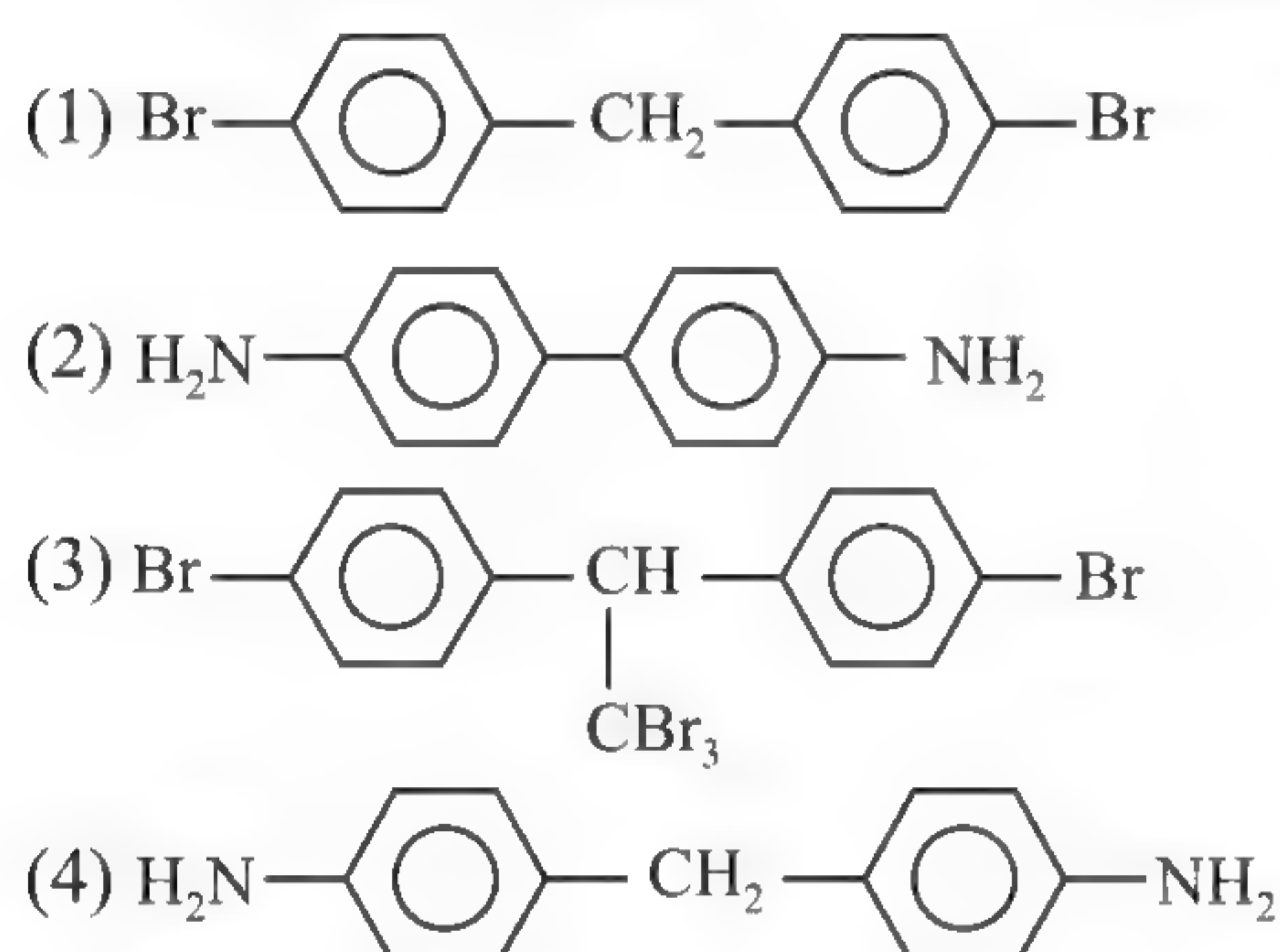
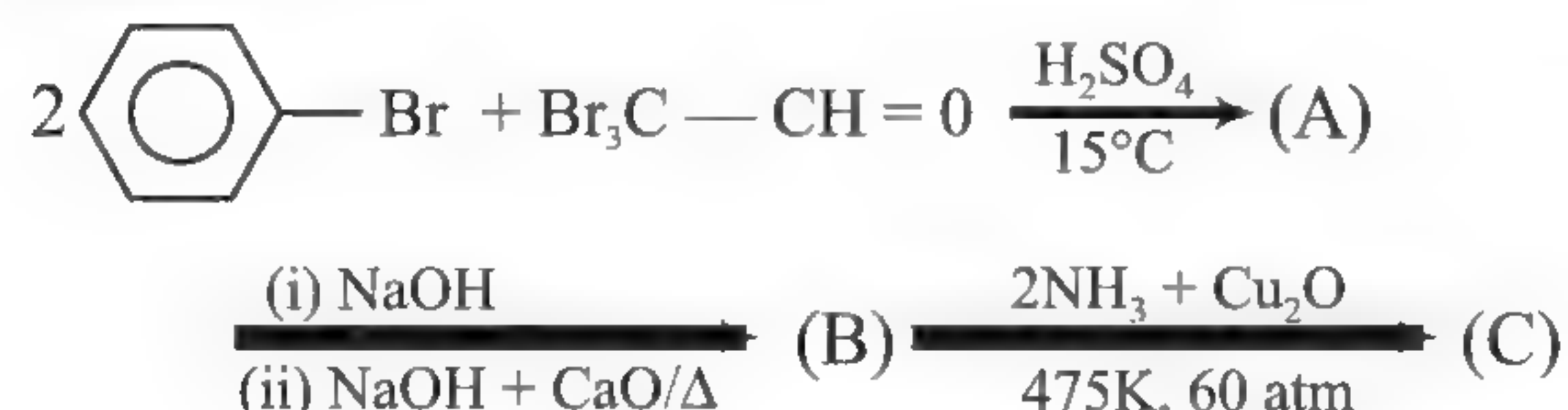
- (1) Chlorobenzene
- (2) Toluene
- (3) Benzyl chloride
- (4) Benzaldehyde



113. Major product for the reaction



114. Identify the final product (C) in the given sequence of reaction.



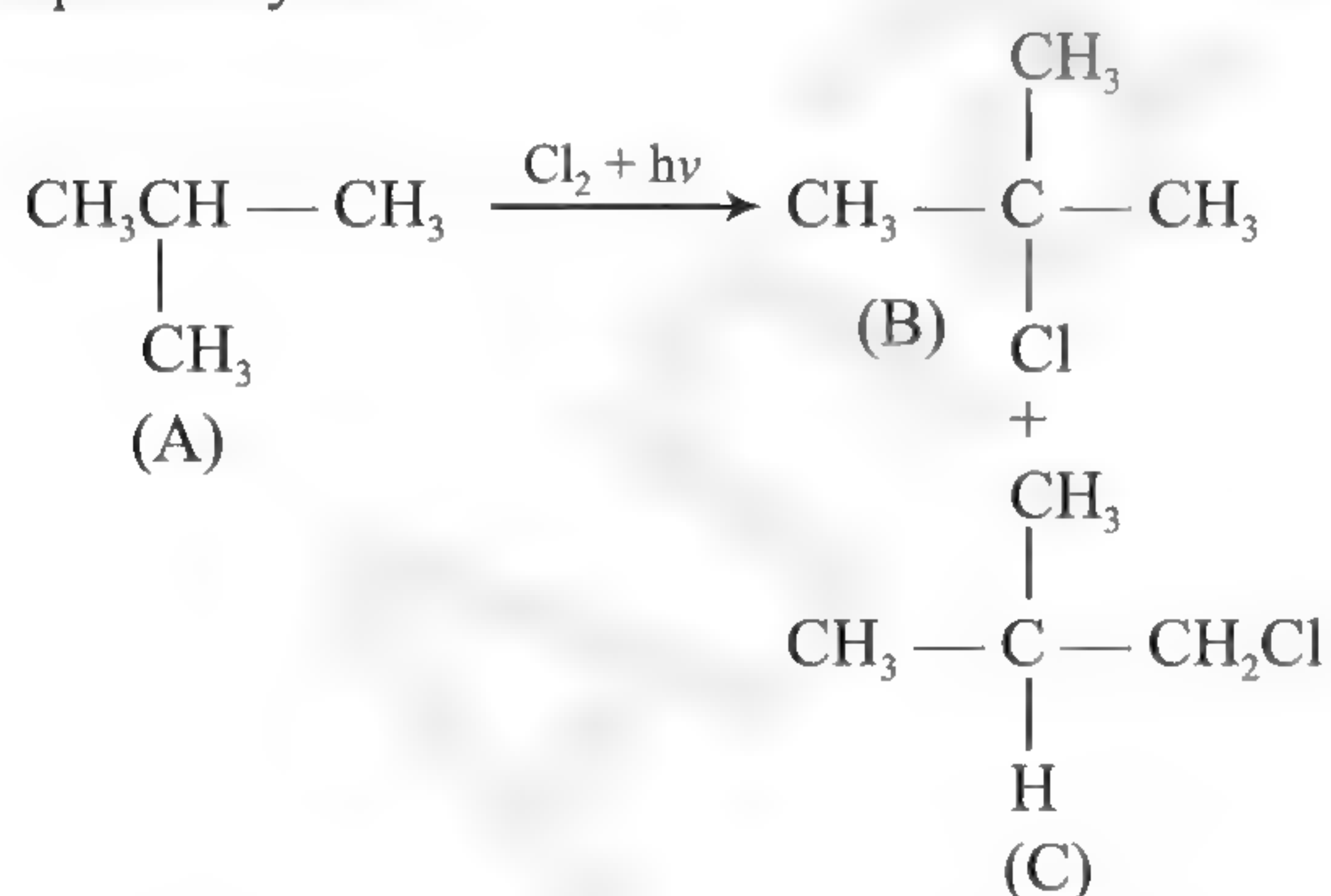
115. Relative reactivity of 1°, 2° and 3° H-atoms to chlorination of alkane is:

- (1) (1.0 : 3.8 : 5) (2) (3.8 : 1.0 : 5.0)
 (3) (5.0 : 1.0 : 3.8) (4) (5.0 : 3.8 : 1.0)

116. Relative reactivity of 1°, 2° and 3° H-atoms to bromination of alkane is:

- (1) (82 : 1600 : 1.0) (2) (1.0 : 1600 : 82)
 (3) (1 : 82 : 1600) (4) None

117. In the following reaction percentage of product (B) and (C) respectively are:

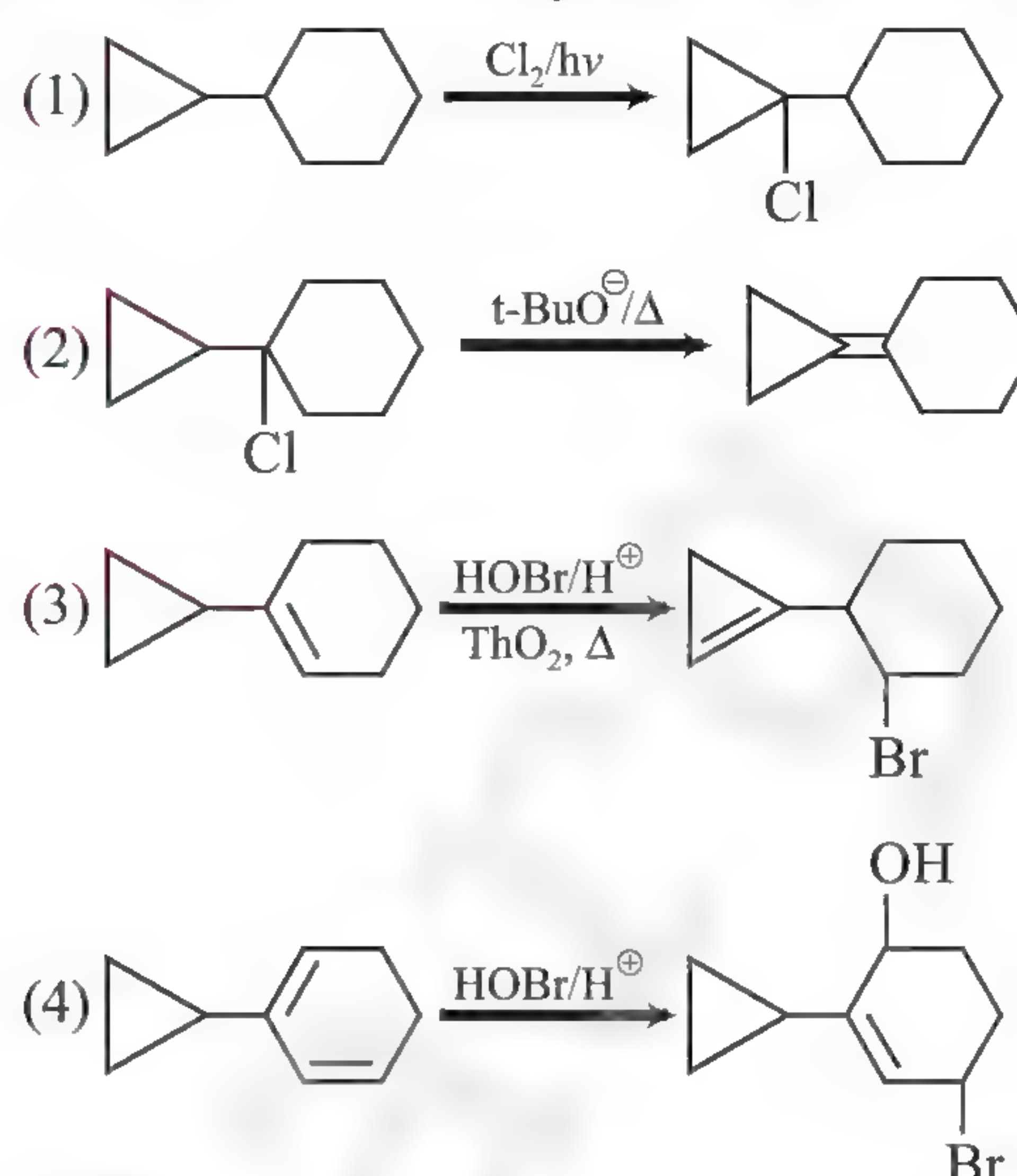


- (1) 35.7 and 64.3 (2) 64.3 and 35.7
 (3) 36.7 and 63.3 (4) 63.3 and 36.7

118. Correct reactivity order towards photochemical bromination of the following compounds is:

- (A) $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$ (B) $\text{CH}_3(\text{CH}_2)_3\text{CH}_3$
 (C) $(\text{CH}_3)_3\text{C}$ (D) CH_3-CH_3
 (1) $\text{A} > \text{B} > \text{C} > \text{D}$ (2) $\text{C} > \text{B} > \text{D} > \text{A}$
 (3) $\text{B} > \text{A} > \text{C} > \text{D}$ (4) $\text{B} > \text{A} > \text{D} > \text{C}$

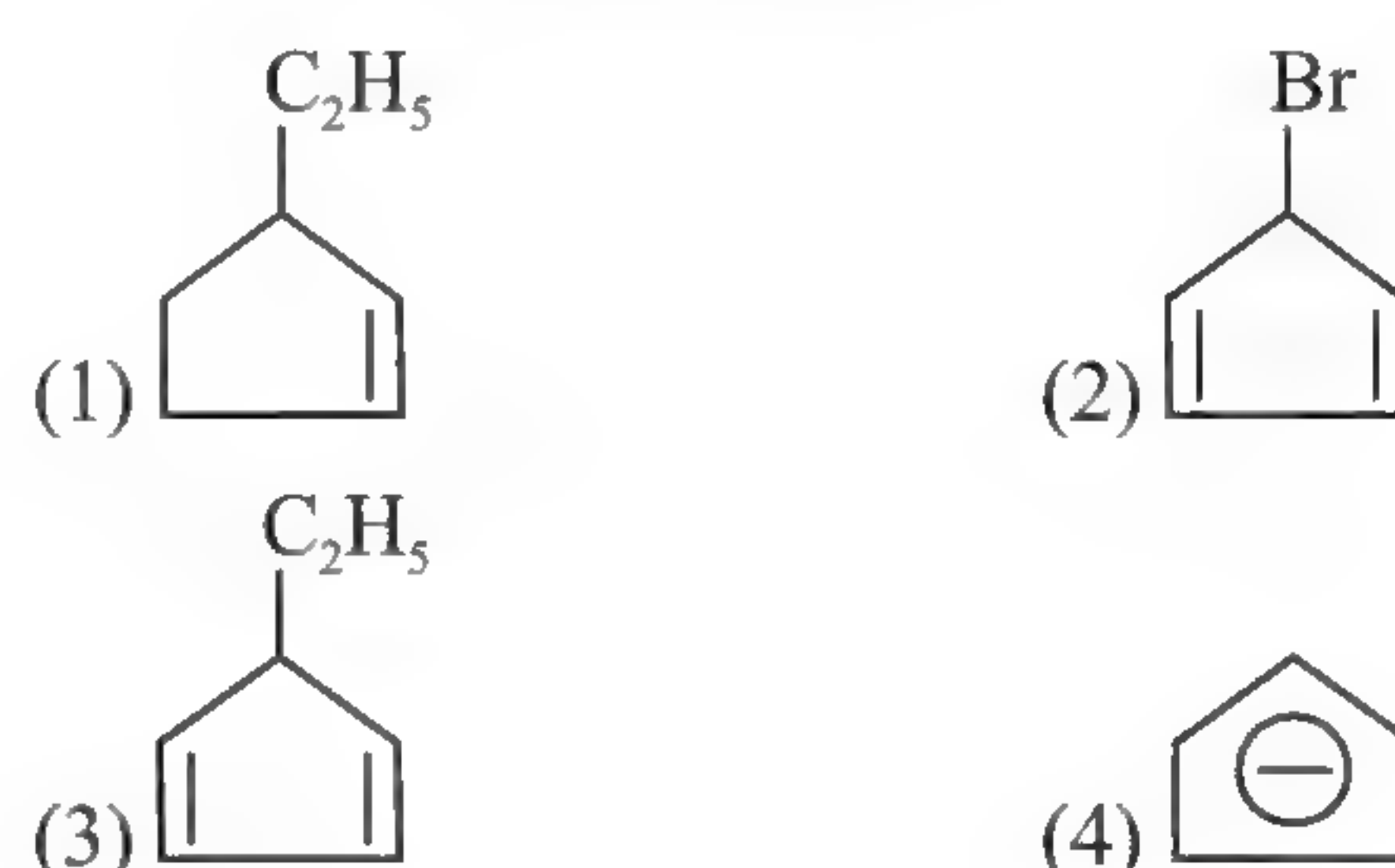
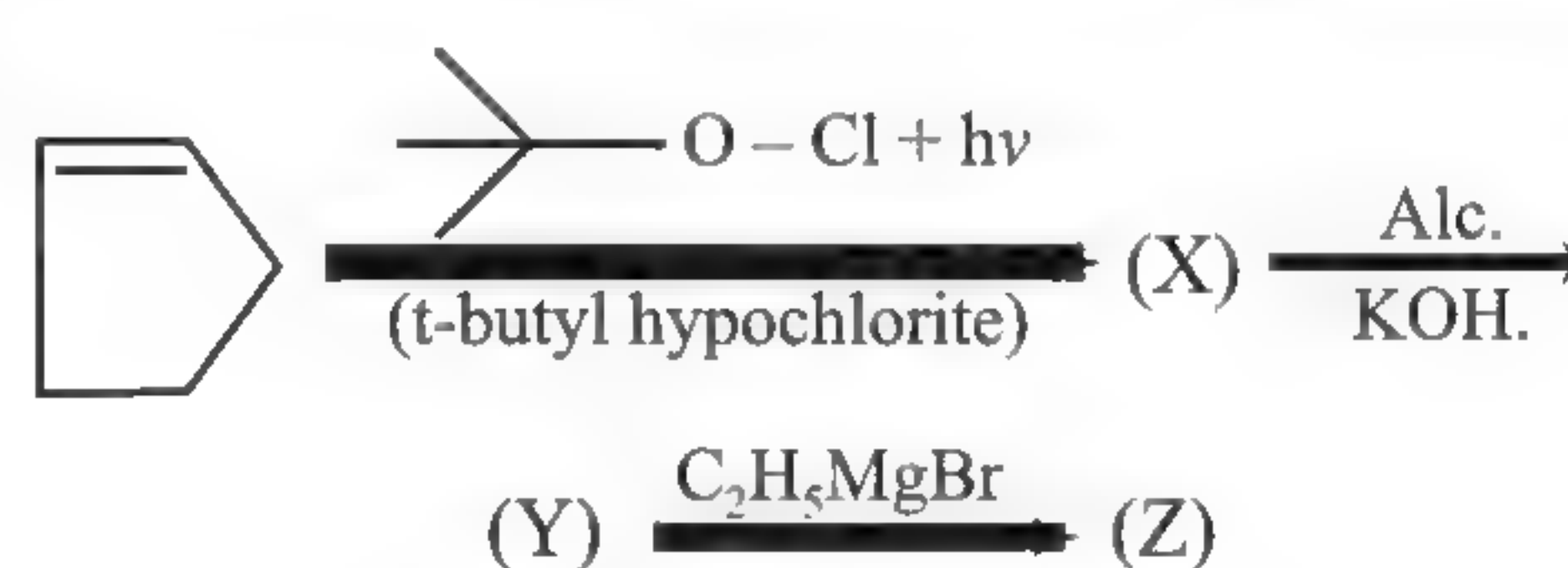
119. Which of the following is correct reaction.



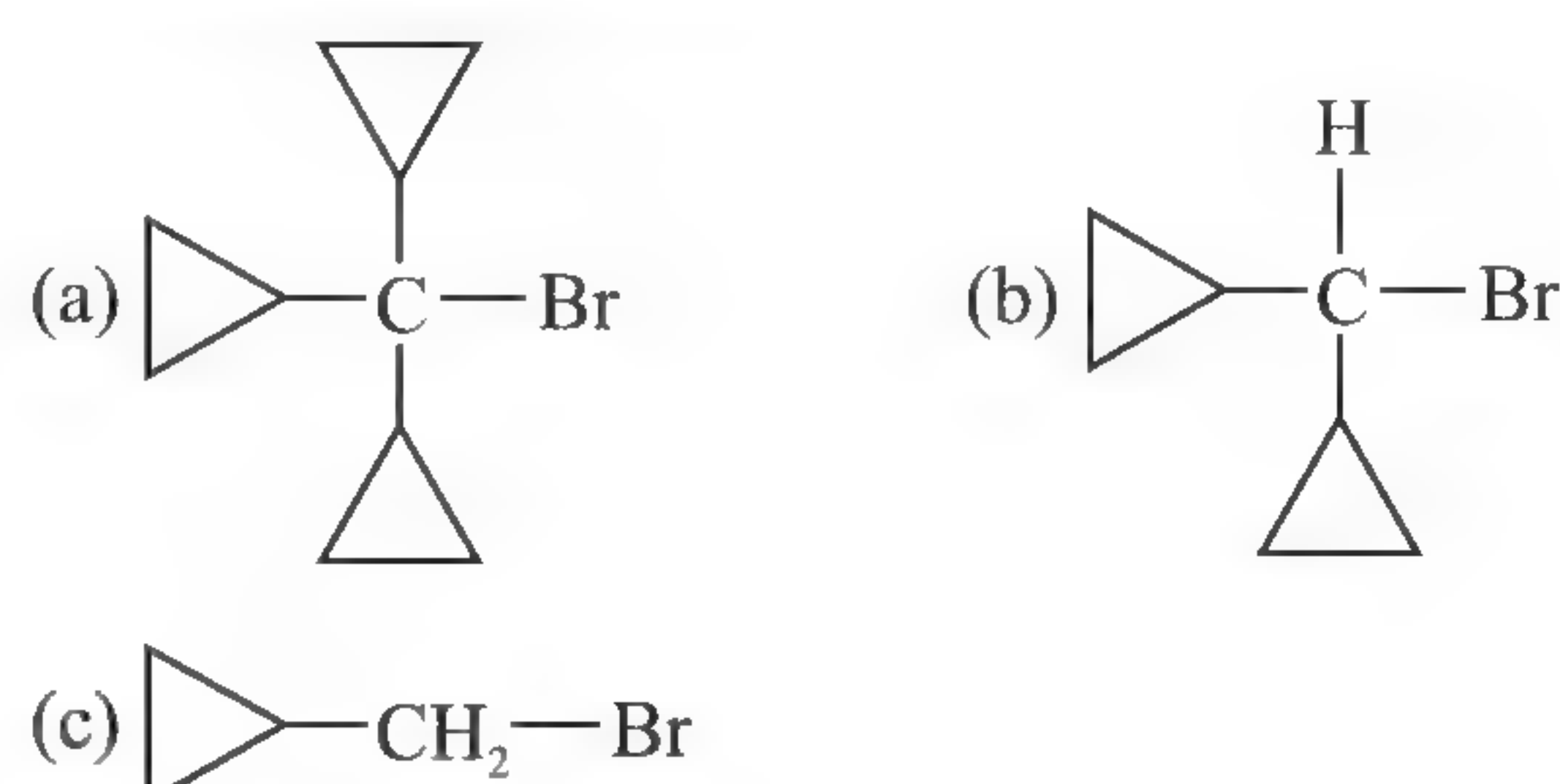
120. Decreasing order of reactivity of $\text{S}_\text{N}1$ reaction for the following compounds is:

- (a) $\text{H}_3\text{CO}-\text{C}_6\text{H}_4-\text{CH}_2\text{Br}$ (b) $\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{CH}_2\text{Br}$
 (c) $\text{C}_6\text{H}_5-\text{CH}_2\text{Br}$ (d) $\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{CH}_2\text{Br}$
 (1) $\text{a} > \text{b} > \text{c} > \text{d}$ (2) $\text{b} > \text{a} > \text{c} > \text{d}$
 (3) $\text{d} > \text{c} > \text{b} > \text{a}$ (4) $\text{a} > \text{b} > \text{d} > \text{c}$

121. The product (Z) in the following reaction is

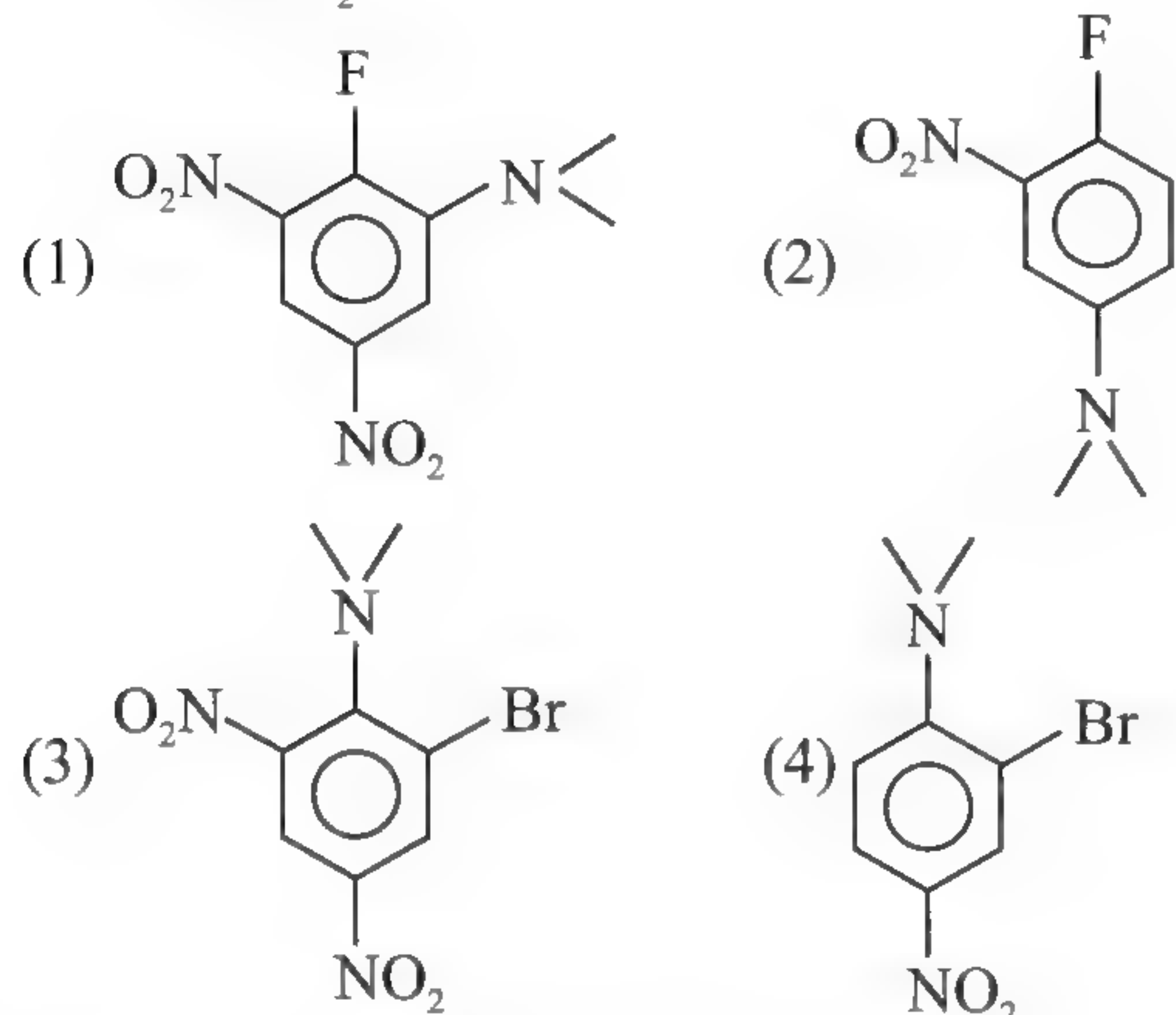
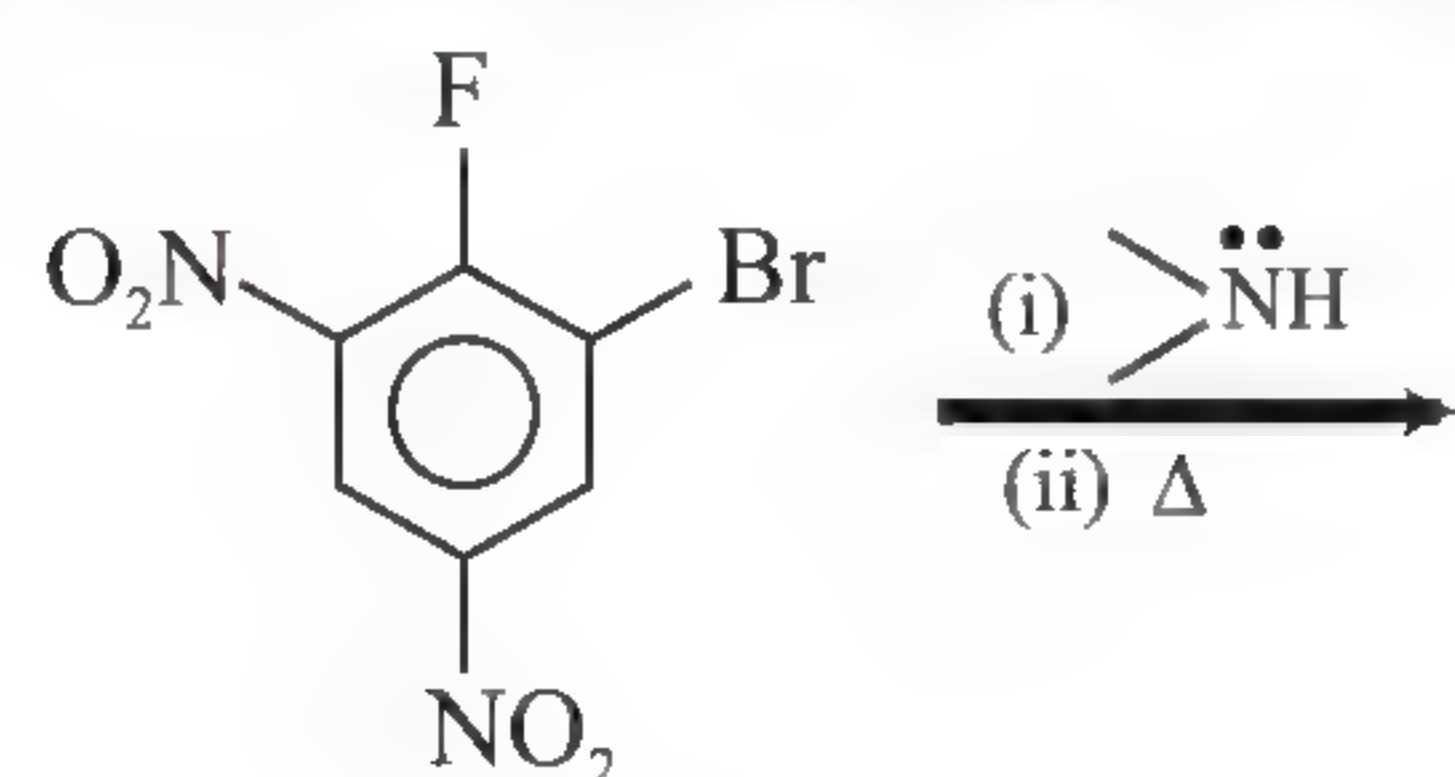


122. Decreasing order of reactivity for $\text{S}_\text{N}1$ reaction for the following compounds is:

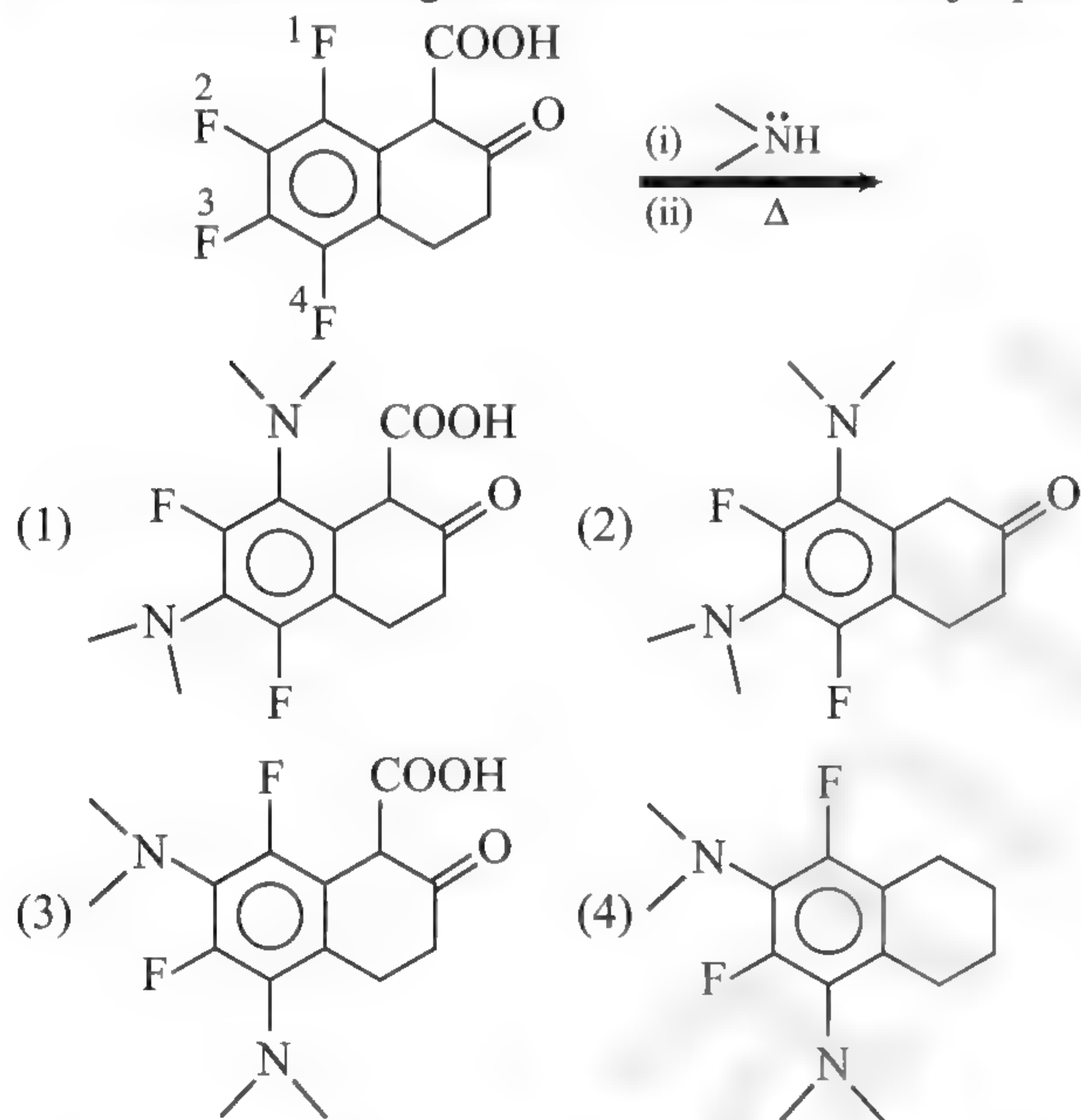


- (1) $\text{a} > \text{b} > \text{c}$ (2) $\text{c} > \text{b} > \text{a}$
 (3) $\text{b} > \text{a} > \text{c}$ (4) $\text{a} > \text{c} > \text{b}$

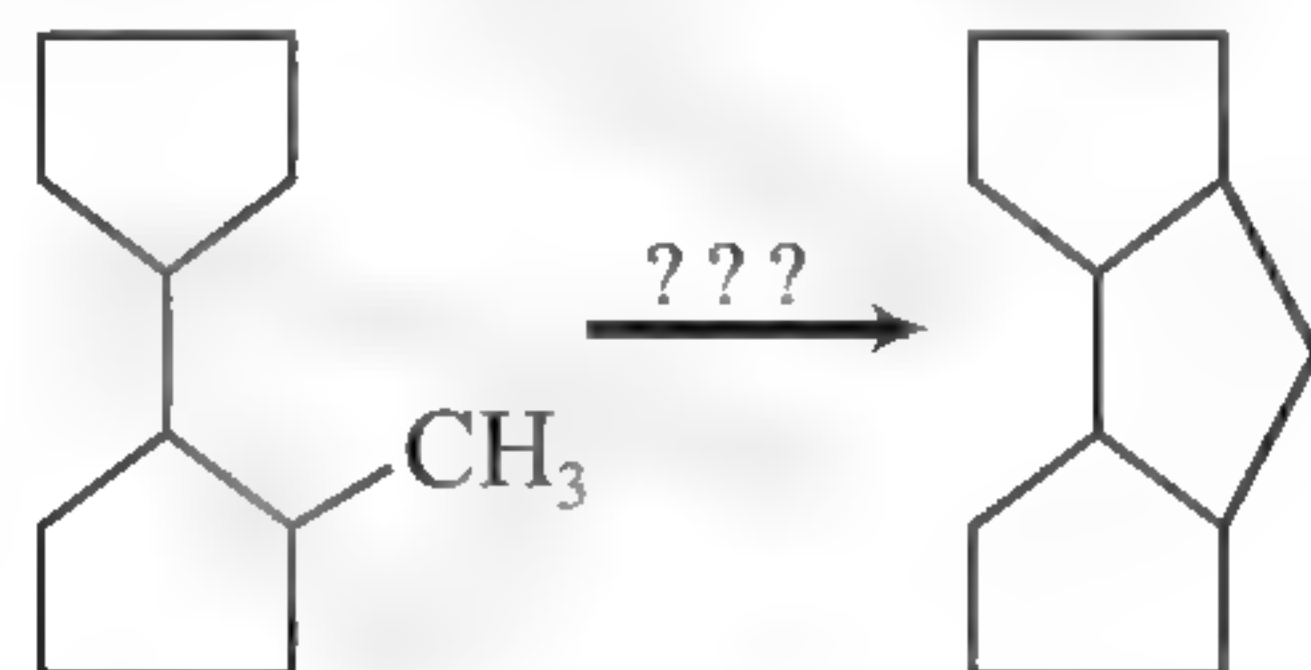
123. Consider the reaction and choose the major product.



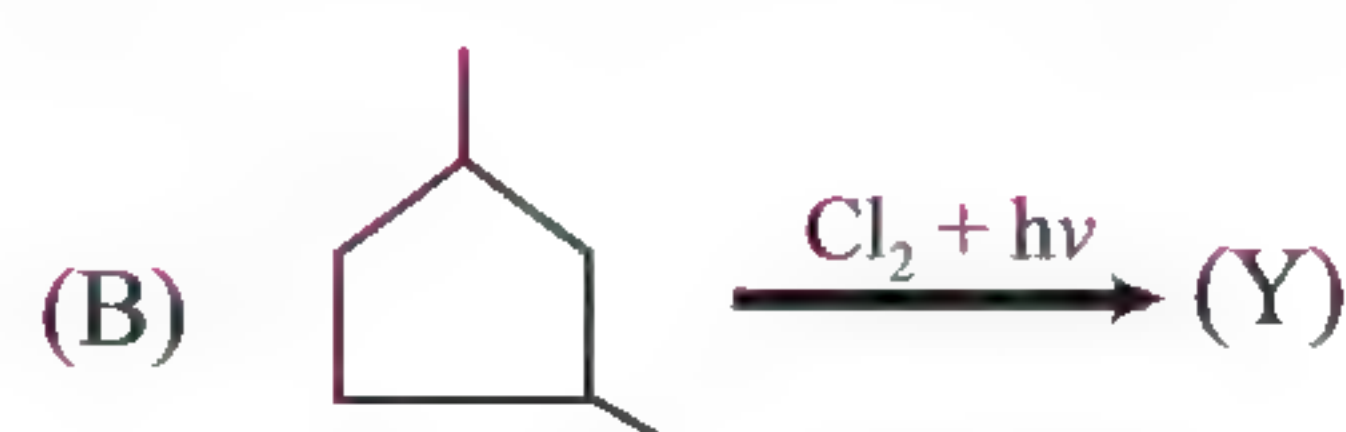
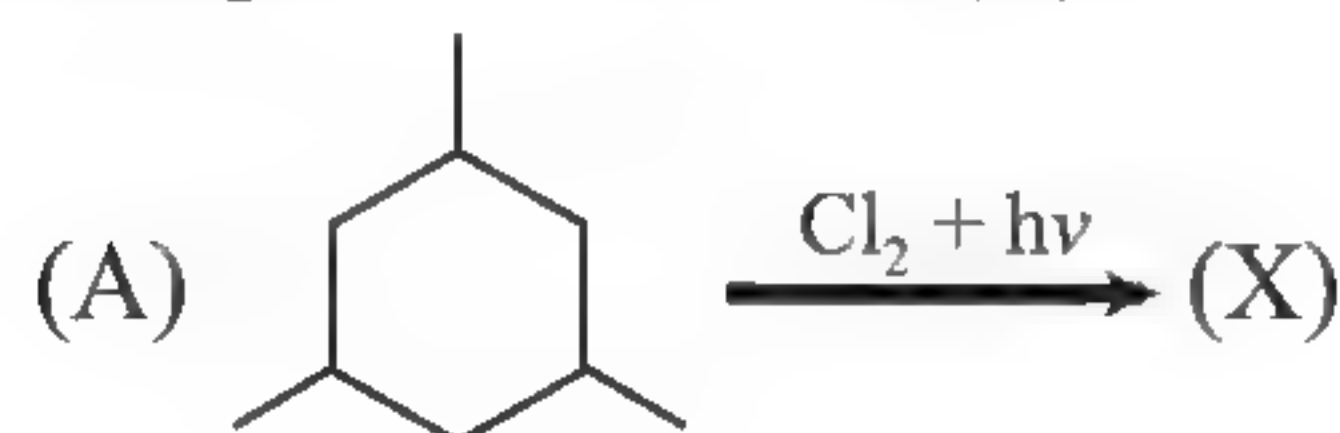
124. Consider the following reaction and choose the major product.



125. Which of the following reagents are required for the following conversion shown below:



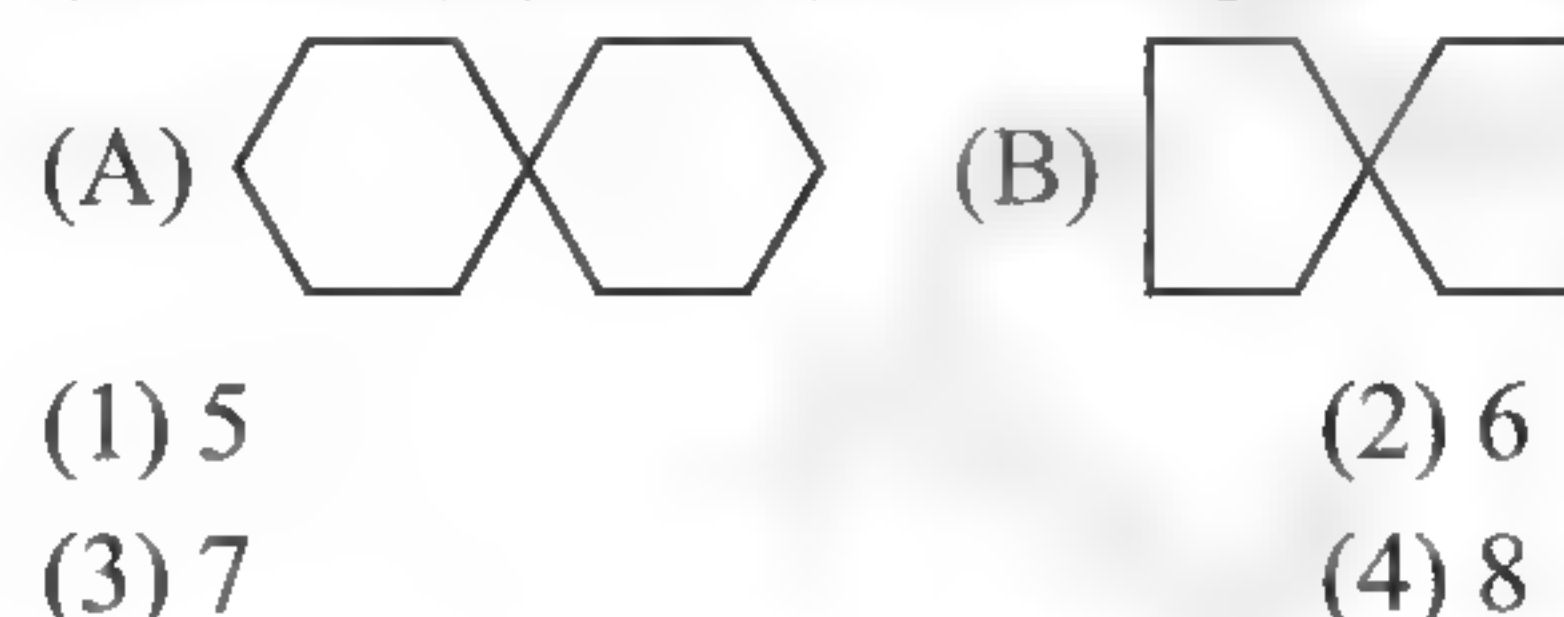
126. The sum of products on monochlorination of the given compounds (A) and (B) are: (excluding stereoisomers)



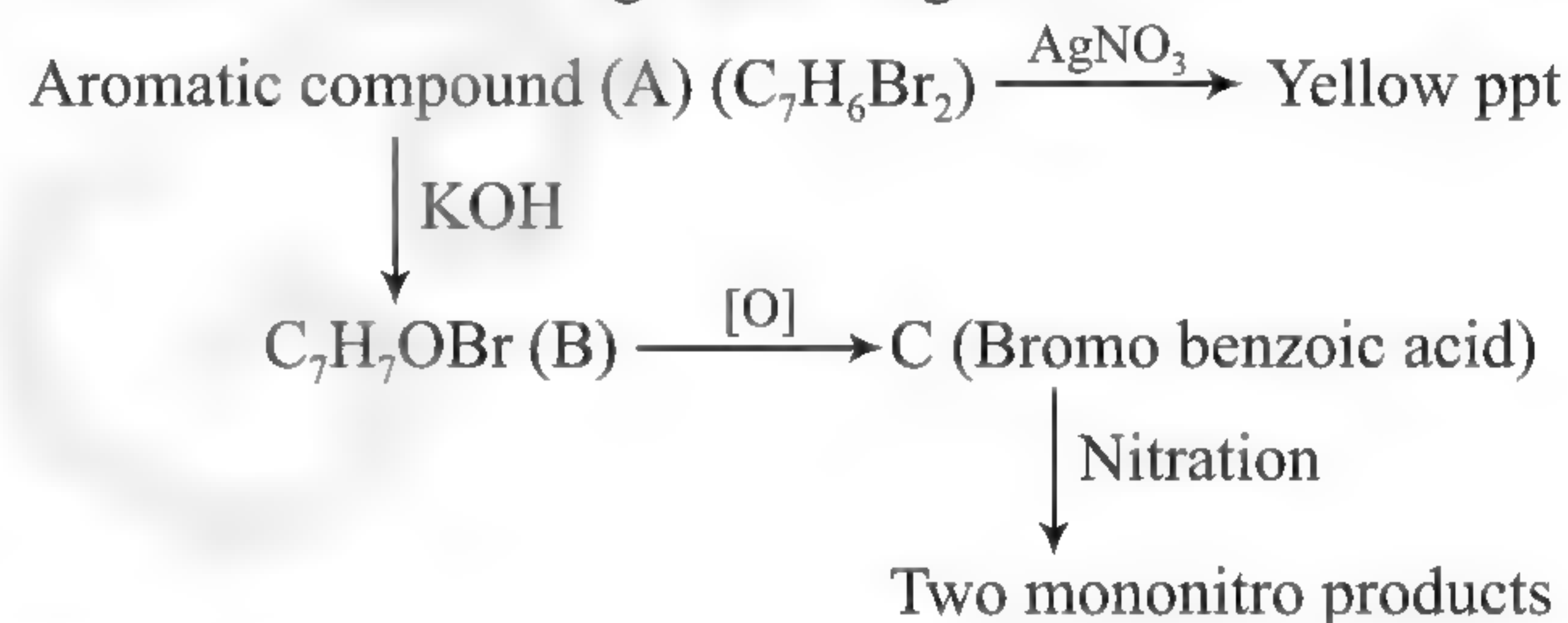
Sum of X + Y is

- (1) 8 (2) 7
(3) 6 (4) 5

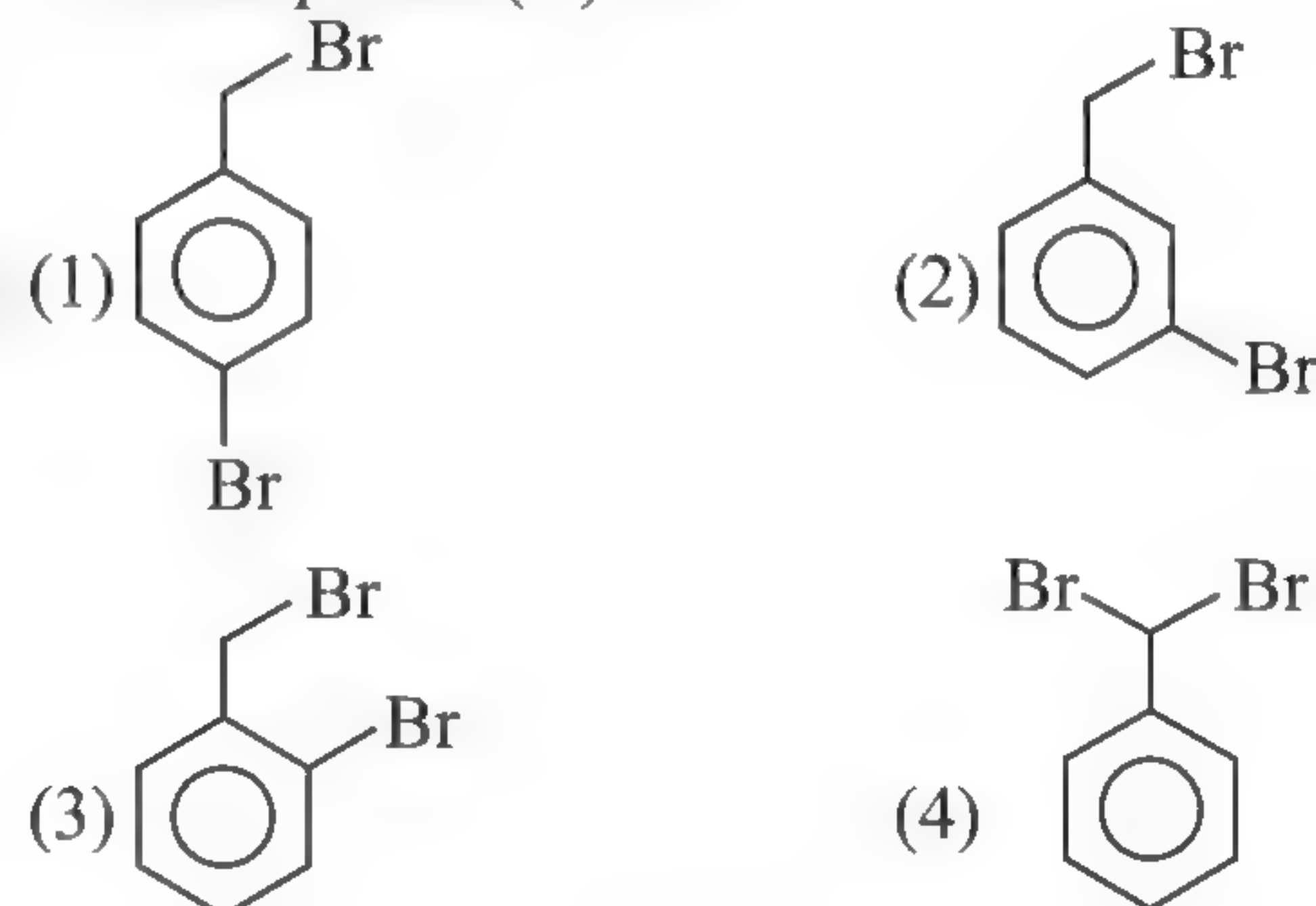
127. The sum of products on monochlorination of the compounds (A) and (B) are: (excluding stereoisomers)



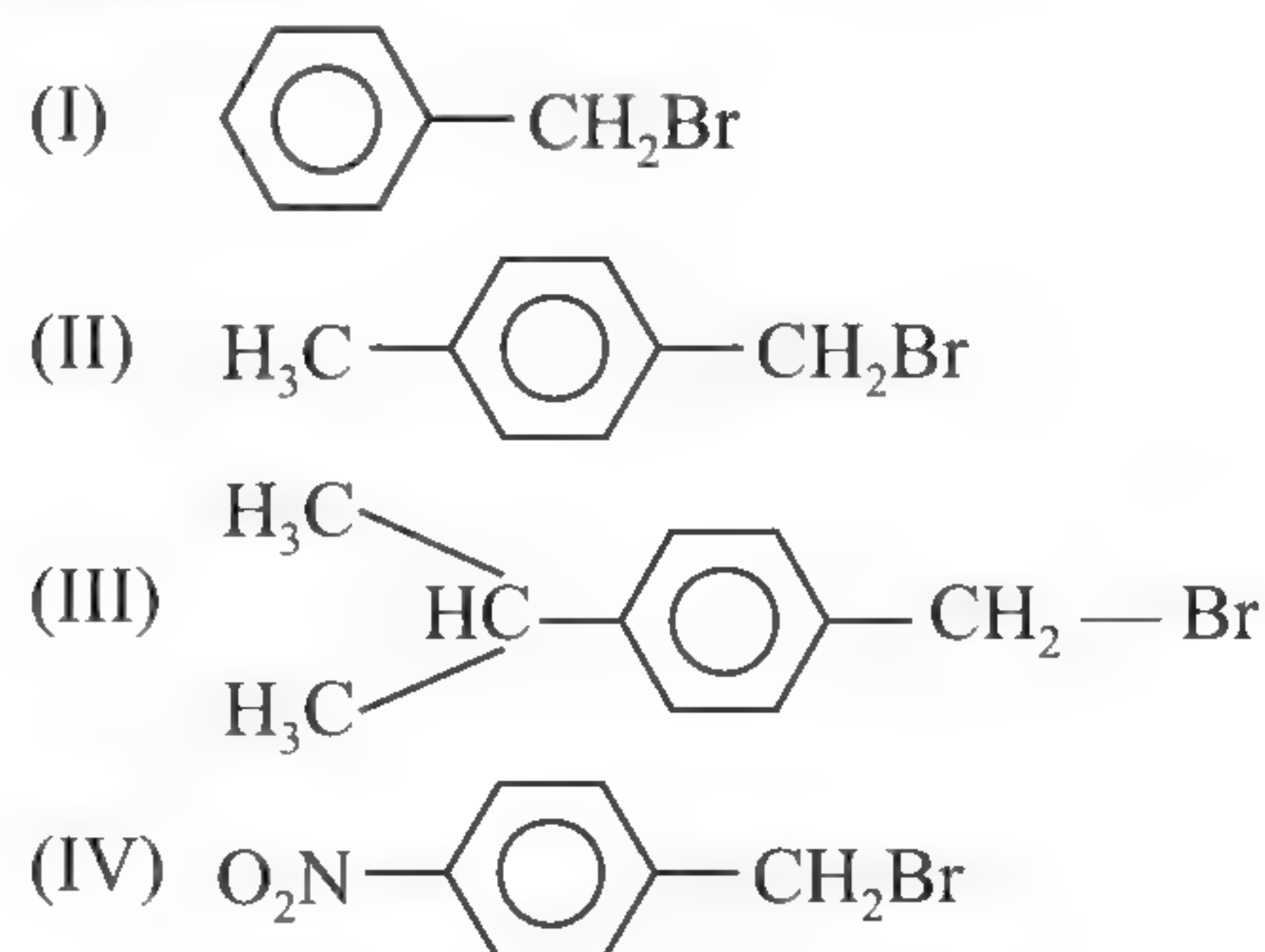
128. Consider the following reactions given below:



The compound (A) is:

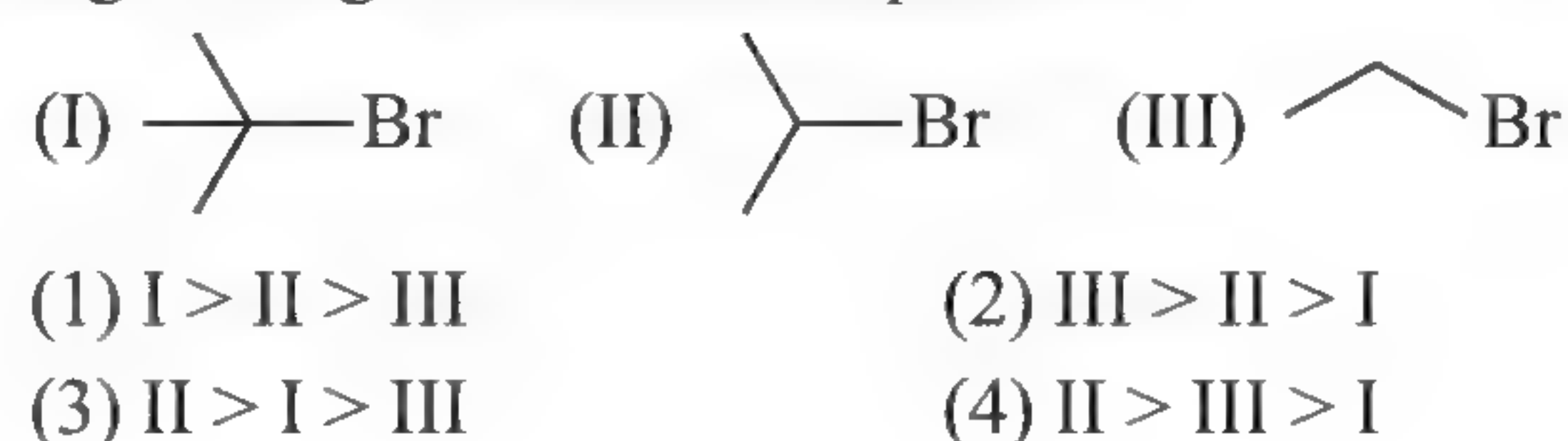


129. Give the order of decreasing rate of hydrolysis for SN^1 reaction.

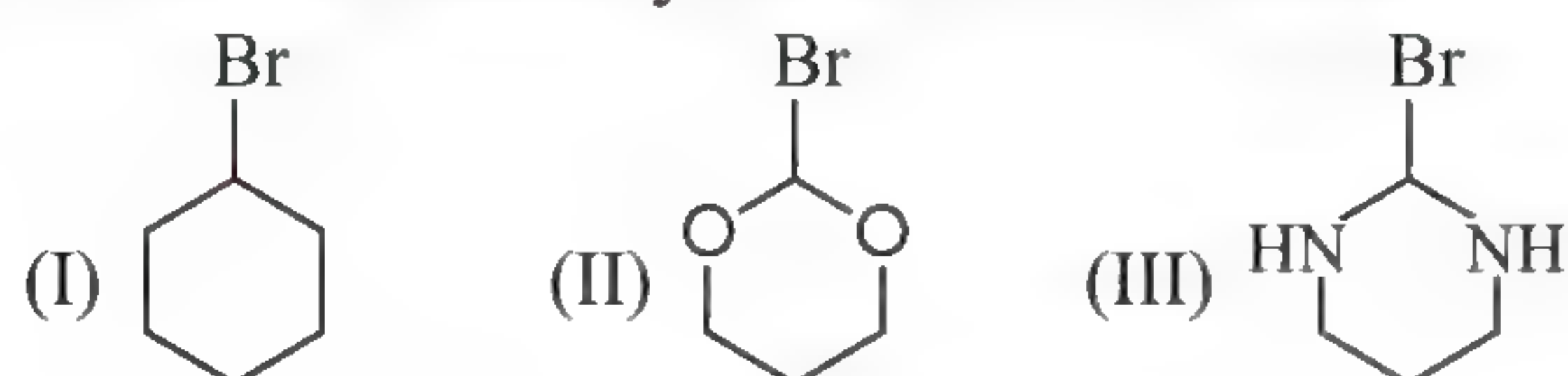


- (1) I > II > III > IV (2) II > III > I > IV
(3) IV > I > II > III (4) I > IV > III > II

130. Give the decreasing order of reactivity with alcoholic AgCN to give substitution product.

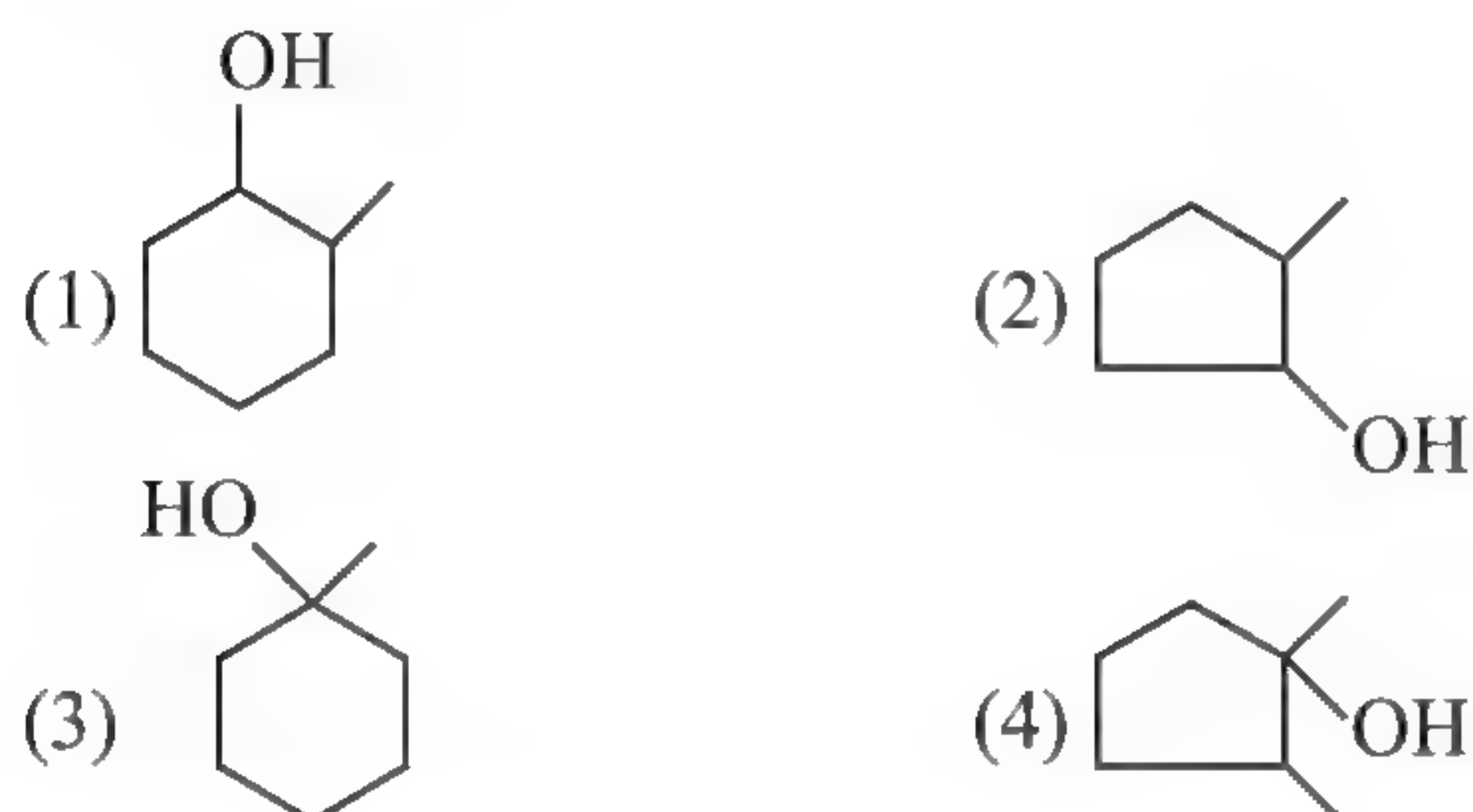
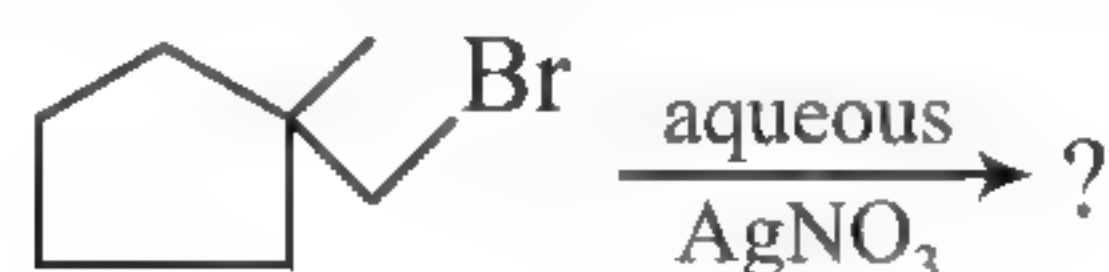


131. The correct reactivity order for S_N1 reaction is:



- (1) I > II > III
(2) III > II > I
(3) II > III > I
(4) III > I > II

132. The major product in the reaction is



133. The decreasing basic order of the following compounds is:

- i. NH_3 ii. PH_3
iii. AsH_3 iv. SbH_3
(1) (i) > (ii) > (iii) > (iv) (2) (iv) > (iii) > (ii) > (i)
(3) (ii) > (i) > (iii) > (iv) (4) (ii) > (i) > (iv) > (iii)

134. The decreasing nucleophilic order of the following compounds is:

- i. NH_3 ii. PH_3
iii. AsH_3 iv. SbH_3
(1) (i) > (ii) > (iii) > (iv) (2) (iv) > (iii) > (ii) > (i)
(3) (ii) > (i) > (iii) > (iv) (4) (ii) > (i) > (iv) > (iii)

135. The decreasing leaving group order of the following compounds is:

- i. NH_3 ii. PH_3
iii. AsH_3 iv. SbH_3
(1) (i) > (ii) > (iii) > (iv) (2) (iv) > (iii) > (ii) > (i)
(3) (ii) > (i) > (iii) > (iv) (4) (ii) > (i) > (iv) > (iii)

136. The decreasing basic order of the following is:

- i. F^\ominus ii. Cl^\ominus
iii. Br^\ominus iv. I^\ominus
(1) (i) > (ii) > (iii) > (iv) (2) (iv) > (iii) > (ii) > (i)
(3) (ii) > (i) > (iii) > (iv) (4) (ii) > (i) > (iv) > (iii)

137. The decreasing nucleophilic order of the following compounds is:

- i. F^\ominus ii. Cl^\ominus
iii. Br^\ominus iv. I^\ominus
(1) (i) > (ii) > (iii) > (iv) (2) (iv) > (iii) > (ii) > (i)
(3) (ii) > (i) > (iii) > (iv) (4) (ii) > (i) > (iv) > (iii)

138. The decreasing leaving group order of the following is:

- i. F^\ominus ii. Cl^\ominus
iii. Br^\ominus iv. I^\ominus
(1) (i) > (ii) > (iii) > (iv) (2) (iv) > (iii) > (ii) > (i)
(3) (ii) > (i) > (iii) > (iv) (4) (ii) > (i) > (iv) > (iii)

139. The decreasing basic order of the following is:

- i. CH_3^\ominus ii. NH_2^\ominus
iii. OH^\ominus iv. F^\ominus
(1) (i) > (ii) > (iii) > (iv) (2) (iv) > (iii) > (ii) > (i)
(3) (ii) > (i) > (iii) > (iv) (4) (ii) > (i) > (iv) > (iii)

140. The decreasing nucleophilic order of the following compounds is:

- i. CH_3^\ominus ii. NH_2^\ominus
iii. OH^\ominus iv. F^\ominus
(1) (i) > (ii) > (iii) > (iv) (2) (iv) > (iii) > (ii) > (i)
(3) (ii) > (i) > (iii) > (iv) (4) (ii) > (i) > (iv) > (iii)

141. The decreasing leaving group order of the following compounds is:

- i. CH_3^\ominus ii. NH_2^\ominus
iii. OH^\ominus iv. F^\ominus
(1) (i) > (ii) > (iii) > (iv) (2) (iv) > (iii) > (ii) > (i)
(3) (ii) > (i) > (iii) > (iv) (4) (ii) > (i) > (iv) > (iii)

142. The decreasing basic order of the following is:

- i. $\text{F}_3\text{CSO}_3^\ominus$ ii. $\text{Cl}_3\text{C}-\text{COO}^\ominus$
iii. PhSO_3^\ominus iv. MeSO_3^\ominus
(1) (i) > (ii) > (iii) > (iv) (2) (iv) > (iii) > (ii) > (i)
(3) (ii) > (iv) > (iii) > (i) (4) (iv) > (ii) > (i) > (iii)

143. The decreasing nucleophilic order of the following compounds is:

- i. $\text{F}_3\text{CSO}_3^\ominus$ ii. $\text{Cl}_3\text{C}-\text{COO}^\ominus$
iii. PhSO_3^\ominus iv. MeSO_3^\ominus
(1) (i) > (ii) > (iii) > (iv) (2) (iv) > (iii) > (ii) > (i)
(3) (ii) > (iv) > (iii) > (i) (4) (iv) > (ii) > (i) > (iii)

144. The decreasing leaving group order of the following compounds is:

- i. $\text{F}_3\text{CSO}_3^\ominus$ ii. $\text{Cl}_3\text{C}-\text{COO}^\ominus$
iii. PhSO_3^\ominus iv. MeSO_3^\ominus
(1) (i) > (ii) > (iii) > (iv) (2) (iv) > (iii) > (ii) > (i)
(3) (iii) > (i) > (ii) > (iv) (4) (i) > (iii) > (iv) > (ii)

145. The decreasing basic order of the following compounds is:

- i. H_2O ii. H_2S
iii. H_2Se iv. H_2Te
(1) (i) > (ii) > (iii) > (iv) (2) (iv) > (iii) > (ii) > (i)
(3) (iii) > (i) > (ii) > (iv) (4) (iv) > (ii) > (i) > (iii)

146. The decreasing nucleophilic order of the following compounds is:

- i. H_2O ii. H_2S
iii. H_2Se iv. H_2Te
(1) (i) > (ii) > (iii) > (iv) (2) (iv) > (iii) > (ii) > (i)
(3) (iii) > (i) > (ii) > (iv) (4) (iv) > (ii) > (i) > (iii)

147. The decreasing leaving group order (fugacity order) of the following compounds is:

- i. H_2O ii. H_2S
iii. H_2Se iv. H_2Te
(1) (i) > (ii) > (iii) > (iv) (2) (iv) > (iii) > (ii) > (i)
(3) (iii) > (i) > (ii) > (iv) (4) (iv) > (ii) > (i) > (iii)

148. The decreasing basic order of the following is:

- | | |
|--------------------------------------|-------------------------------|
| i. CH_3^\ominus | ii. OH^\ominus |
| iii. $\text{CH}_3\text{COO}^\ominus$ | iv. H_2O |
| (1) (i) > (ii) > (iii) > (iv) | (2) (iv) > (iii) > (ii) > (i) |
| (3) (iii) > (ii) > (i) > (iv) | (4) (iii) > (ii) > (iv) > (i) |

149. The decreasing nucleophilic order of the following compounds is:

- | | |
|--------------------------------------|-------------------------------|
| i. CH_3^\ominus | ii. OH^\ominus |
| iii. $\text{CH}_3\text{COO}^\ominus$ | iv. H_2O |
| (1) (i) > (ii) > (iii) > (iv) | (2) (iv) > (iii) > (ii) > (i) |
| (3) (iii) > (ii) > (i) > (iv) | (4) (iii) > (ii) > (iv) > (i) |

150. The decreasing fugacity order of the following compounds is:

- | | |
|--------------------------------------|-------------------------------|
| i. CH_3^\ominus | ii. OH^\ominus |
| iii. $\text{CH}_3\text{COO}^\ominus$ | iv. H_2O |
| (1) (i) > (ii) > (iii) > (iv) | (2) (iv) > (iii) > (ii) > (i) |
| (3) (iii) > (ii) > (i) > (iv) | (4) (iii) > (ii) > (iv) > (i) |

151. The decreasing basic order of the following is:

- | | |
|---|---|
| i. PhSO_3^\ominus | ii. $\text{C}_2\text{H}_5\text{SO}_3^\ominus$ |
| iii. $\text{C}_2\text{H}_5\text{COO}^\ominus$ | iv. CN^\ominus |
| v. OH^\ominus | |
| (1) (v) > (iv) > (iii) > (ii) > (i) | |
| (2) (i) > (ii) > (iii) > (iv) > (v) | |
| (3) (iv) > (v) > (iii) > (ii) > (i) | |
| (4) (i) > (ii) > (iii) > (v) > (iv) | |

152. The decreasing nucleophilic order of the following compounds is:

- | | |
|---|---|
| i. PhSO_3^\ominus | ii. $\text{C}_2\text{H}_5\text{SO}_3^\ominus$ |
| iii. $\text{C}_2\text{H}_5\text{COO}^\ominus$ | iv. CN^\ominus |
| v. OH^\ominus | |
| (1) (v) > (iv) > (iii) > (ii) > (i) | |
| (2) (i) > (ii) > (iii) > (iv) > (v) | |
| (3) (iv) > (v) > (iii) > (ii) > (i) | |
| (4) (i) > (ii) > (iii) > (v) > (iv) | |

153. The decreasing fugacity order of the following compounds is:

- | | |
|---|---|
| i. PhSO_3^\ominus | ii. $\text{C}_2\text{H}_5\text{SO}_3^\ominus$ |
| iii. $\text{C}_2\text{H}_5\text{COO}^\ominus$ | iv. CN^\ominus |
| v. OH^\ominus | |
| (1) (v) > (iv) > (iii) > (ii) > (i) | |
| (2) (i) > (ii) > (iii) > (iv) > (v) | |
| (3) (iv) > (v) > (iii) > (ii) > (i) | |
| (4) (i) > (ii) > (iii) > (v) > (iv) | |

154. The decreasing basic order of the following is:

- | | |
|---------------------------|---------------------------|
| i. CN^\ominus | ii. OH^\ominus |
| iii. OMe^\ominus | iv. CH_3^\ominus |
| v. H^\ominus | |

- | |
|-------------------------------------|
| (1) (v) > (iv) > (iii) > (ii) > (i) |
| (2) (i) > (ii) > (iii) > (iv) > (v) |
| (3) (iv) > (v) > (ii) > (iii) > (i) |
| (4) (i) > (ii) > (iii) > (v) > (iv) |

155. The decreasing nucleophilic order of the following compounds is:

- | | |
|-------------------------------------|---------------------------|
| i. CN^\ominus | ii. OH^\ominus |
| iii. OMe^\ominus | iv. CH_3^\ominus |
| v. H^\ominus | |
| (1) (v) > (iv) > (iii) > (ii) > (i) | |
| (2) (i) > (ii) > (iii) > (iv) > (v) | |
| (3) (iv) > (v) > (ii) > (iii) > (i) | |
| (4) (i) > (ii) > (iii) > (v) > (iv) | |

156. The decreasing fugacity order of the following compounds is:

- | | |
|-------------------------------------|---------------------------|
| i. CN^\ominus | ii. OH^\ominus |
| iii. OMe^\ominus | iv. CH_3^\ominus |
| v. H^\ominus | |
| (1) (v) > (iv) > (iii) > (ii) > (i) | |
| (2) (i) > (ii) > (iii) > (iv) > (v) | |
| (3) (iv) > (v) > (ii) > (iii) > (i) | |
| (4) (i) > (ii) > (iii) > (v) > (iv) | |

157. The decreasing basic order of the following is:

- | | |
|---------------------------------------|-------------------------------|
| i. $\text{Me}_2\text{N}-\text{NMe}_2$ | ii. $\text{MeNH}-\text{NHMe}$ |
| iii. $\text{H}_2\text{N}-\text{NH}_2$ | iv. NH_3 |
| (1) (i) > (ii) > (iii) > (iv) | (2) (iv) > (iii) > (ii) > (i) |
| (3) (iv) > (iii) > (i) > (ii) | (4) (iii) > (iv) > (ii) > (i) |

158. Decreasing nucleophilic order of the following is:

- | | |
|---------------------------------------|-------------------------------|
| i. $\text{Me}_2\text{N}-\text{NMe}_2$ | ii. $\text{MeNH}-\text{NHMe}$ |
| iii. $\text{H}_2\text{N}-\text{NH}_2$ | iv. NH_3 |
| (1) (i) > (ii) > (iii) > (iv) | (2) (iv) > (iii) > (ii) > (i) |
| (3) (iv) > (iii) > (i) > (ii) | (4) (iii) > (iv) > (ii) > (i) |

159. The decreasing fugacity order of the following is:

- | | |
|---------------------------------------|-------------------------------|
| i. $\text{Me}_2\text{N}-\text{NMe}_2$ | ii. $\text{MeNH}-\text{NHMe}$ |
| iii. $\text{H}_2\text{N}-\text{NH}_2$ | iv. NH_3 |
| (1) (i) > (ii) > (iii) > (iv) | (2) (iv) > (iii) > (ii) > (i) |
| (3) (iv) > (iii) > (i) > (ii) | (4) (iii) > (iv) > (ii) > (i) |

160. The decreasing order of SN^2 reactivity of alkoxide nucleophiles:

- | | |
|--------------------------------------|-------------------------------------|
| i. $\text{Me}_3\text{CO}^\ominus$ | ii. MeO^\ominus |
| iii. $\text{MeCH}_2\text{O}^\ominus$ | iv. $\text{Me}_2\text{CHO}^\ominus$ |



- | |
|-------------------------------------|
| (1) (i) > (iv) > (v) > (iii) > (ii) |
| (2) (ii) > (iii) > (v) > (iv) > (i) |
| (3) (i) > (v) > (iv) > (iii) > (ii) |
| (4) (ii) > (iii) > (iv) > (v) > (i) |

161. Which of the following reactions is incorrect for the preparation of 100% cumene?

- (1) Benzene + Propene $\xrightarrow[\text{(ii) } \text{O}_2/\text{OH}^-, 130^\circ\text{C}]{\text{(i) } \text{H}_2\text{SO}_4}$
- (2) Benzene + Isopropyl bromide $\xrightarrow[\text{(ii) } \text{O}_2/\text{OH}^-, 130^\circ\text{C}]{\text{(i) Anhyd. AlCl}_3}$
- (3) Benzene + Isopropyl alcohol $\xrightarrow[\text{(ii) } \text{O}_2/\text{OH}^-, 130^\circ\text{C}]{\text{(i) BF}_3}$
- (4) Benzene + Propanol $\xrightarrow[\text{(ii) } \text{O}_2/\text{OH}^-, 130^\circ\text{C}]{\text{(i) BF}_3}$

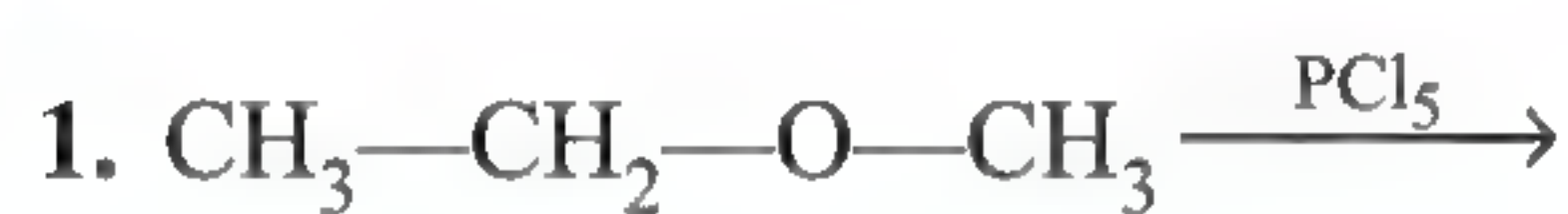
162. $\text{O}=\text{C}_6\text{H}_4=\text{O} + \text{HBr} \longrightarrow (\text{A})$

(A) would be:

- (1) $\text{O}=\text{C}_6\text{H}_4(\text{Br})=\text{O}$ (2) $\text{Br}-\text{C}_6\text{H}_4-\text{OH}$
- (3) $\text{HO}-\text{C}_6\text{H}_3(\text{Br})-\text{OH}$ (4) $\text{Br}-\text{C}_6\text{H}_3(\text{OH})-\text{OH}$

Multiple Correct Answers Type

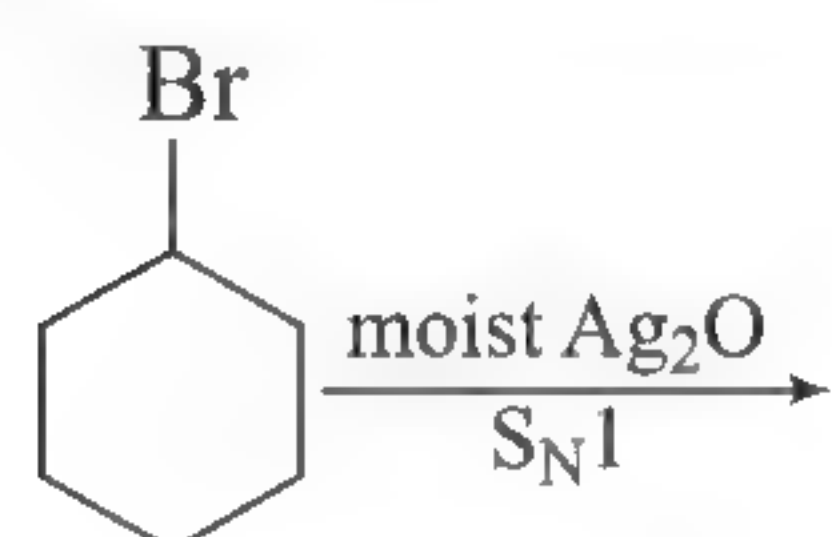
Reactions, properties of Alkyl and Aryl Halides



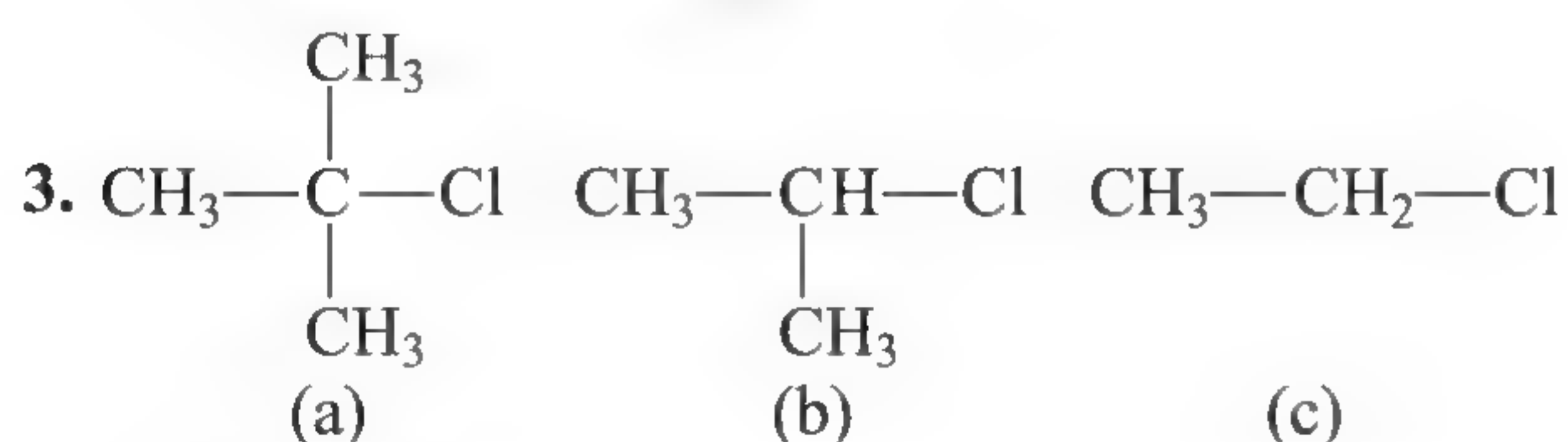
Product are:

- (1) CH_3-Cl (2) $\text{Et}-\text{Cl}$
- (3) $\text{CH}_3-\text{CH}_2-\text{Cl}$ (4) $\text{CH}_3-\text{CH}_2-\text{O}-\text{CH}_2-\text{Cl}$

2. Product in the following reaction is:



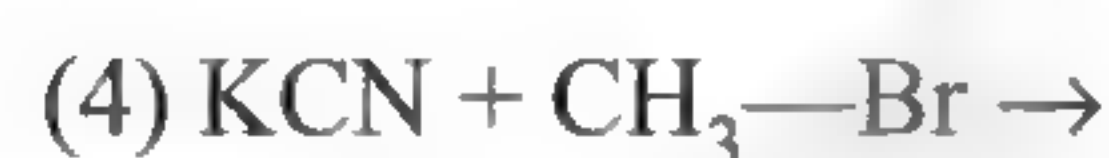
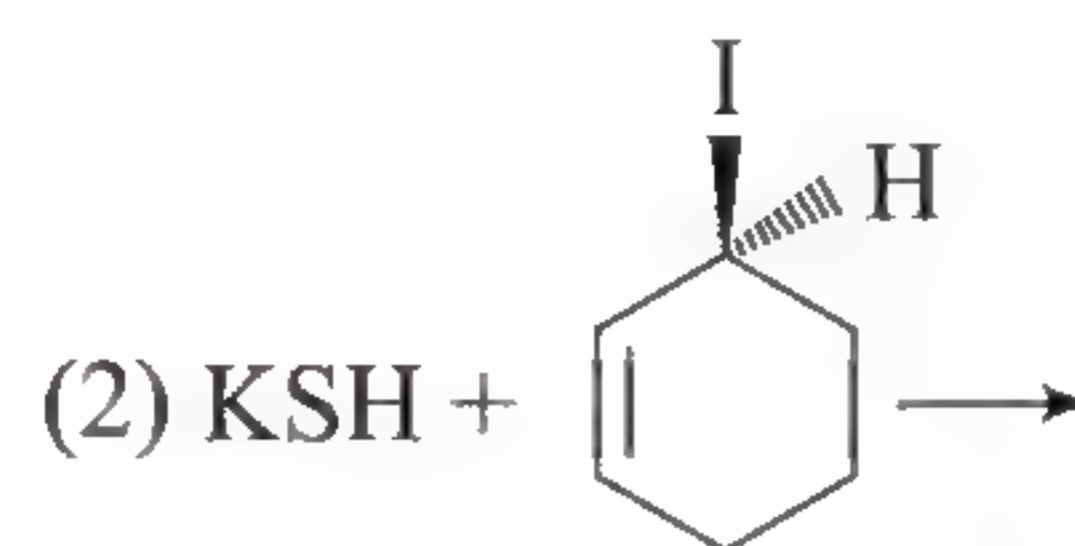
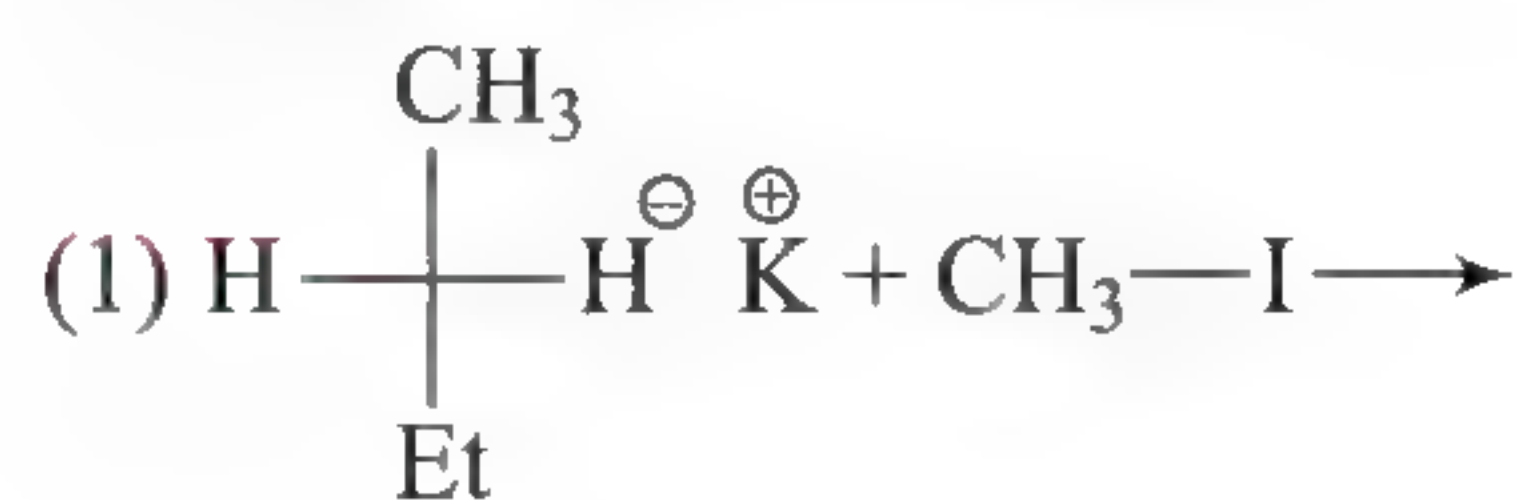
- (1) Cyclohexanol (2) Cyclohexylmethanol
- (3) 2-methylcyclohexanol (4) 2-methylcyclohexylmethanol



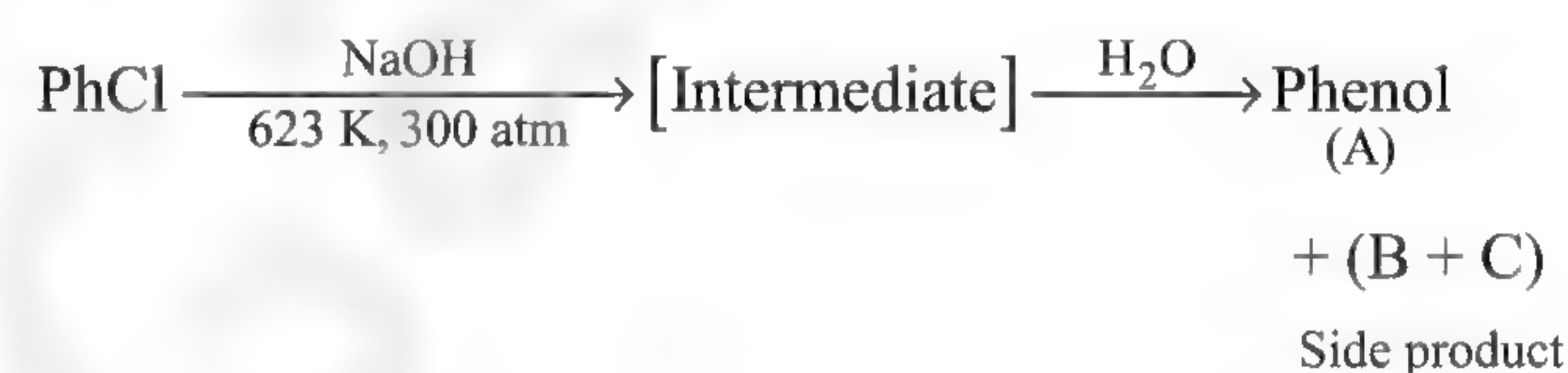
Correct statement is:

- (1) rate of $\text{S}_\text{N}1$ $a > b > c$ (2) rate of $\text{S}_\text{N}2$ $a > b > c$
- (3) rate of $\text{E}2$ $a > b > c$ (4) rate of $\text{E}1$ $a > b > c$

4. In which of the following reactions inversion of configuration will take place?

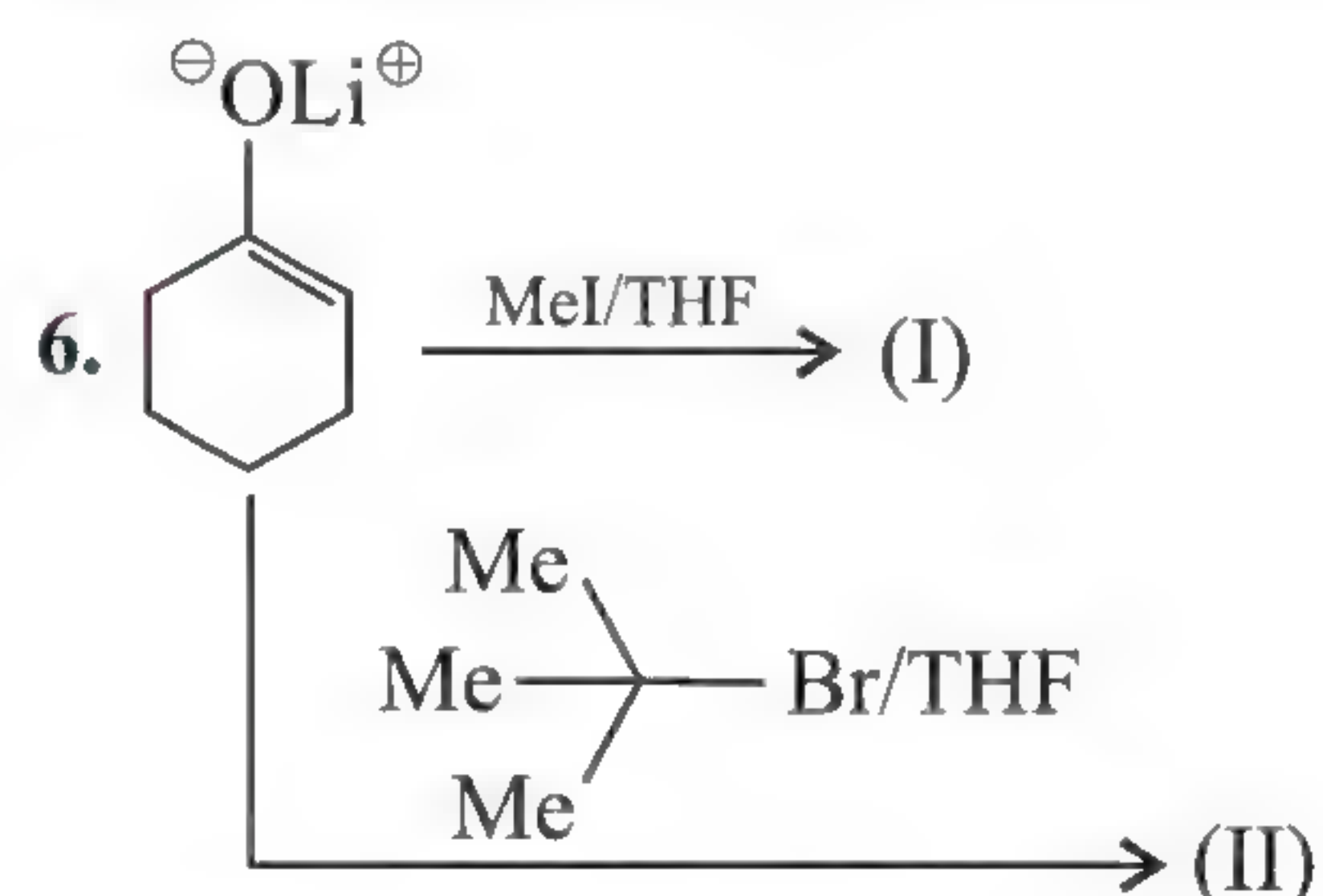


5. In Dow's process for the manufacture of phenol, PhCl is fused with NaOH at elevated temperature under pressure.

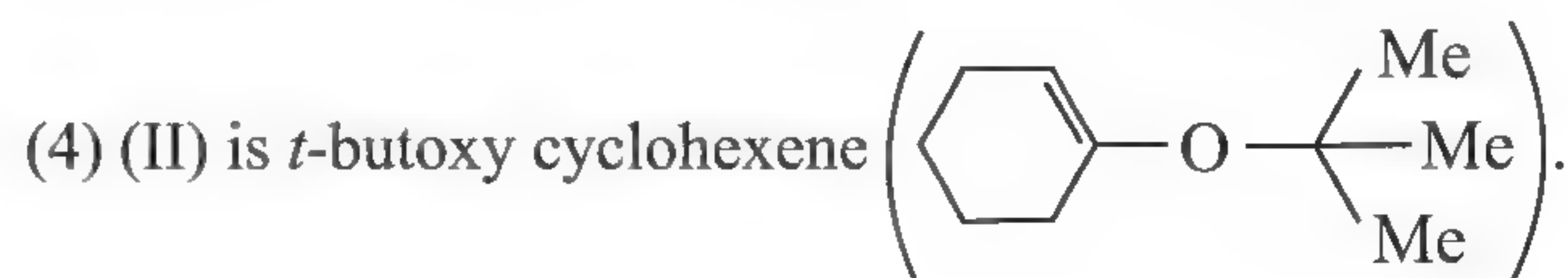
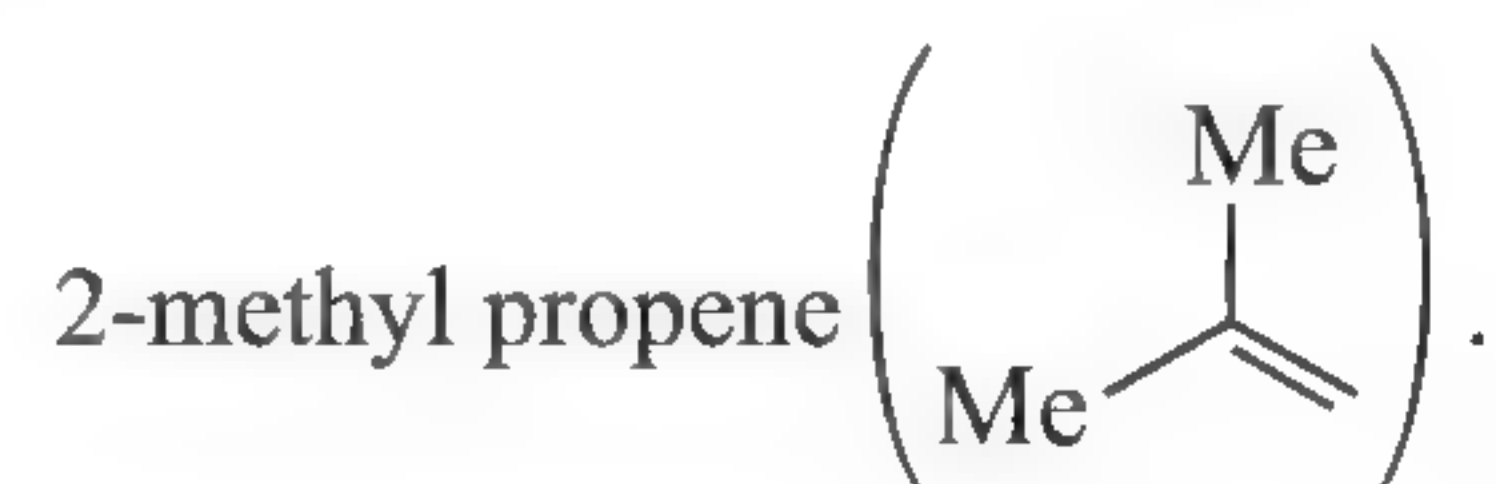
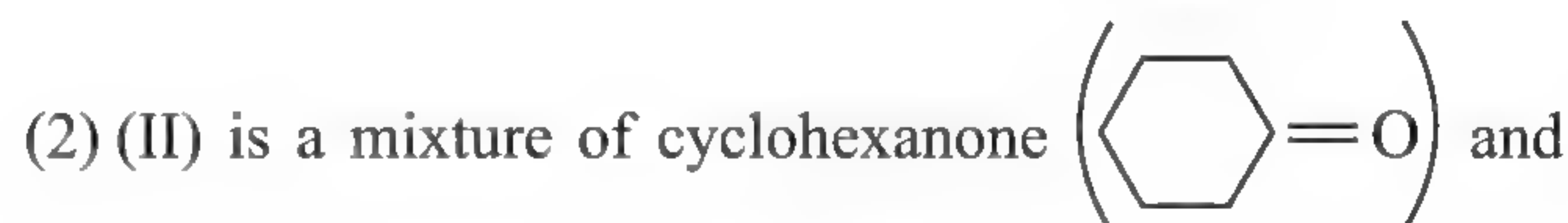
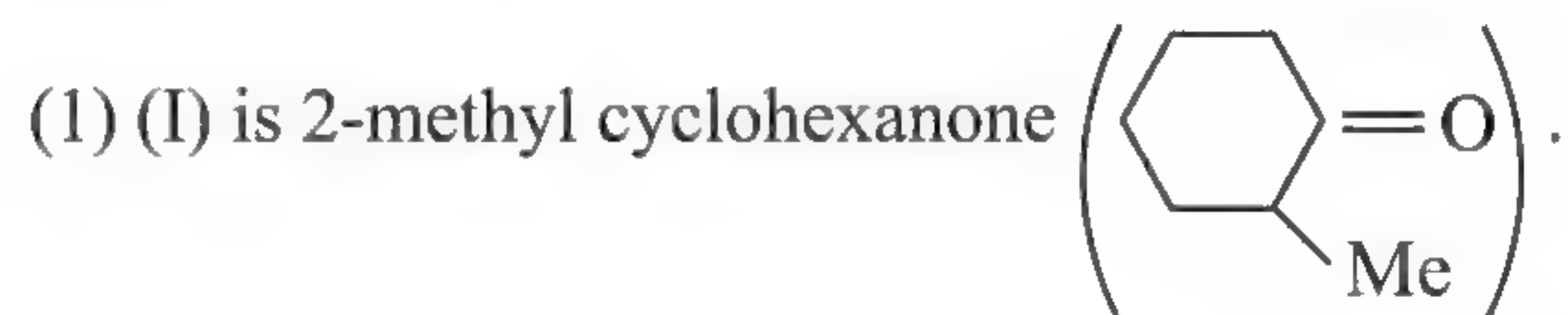


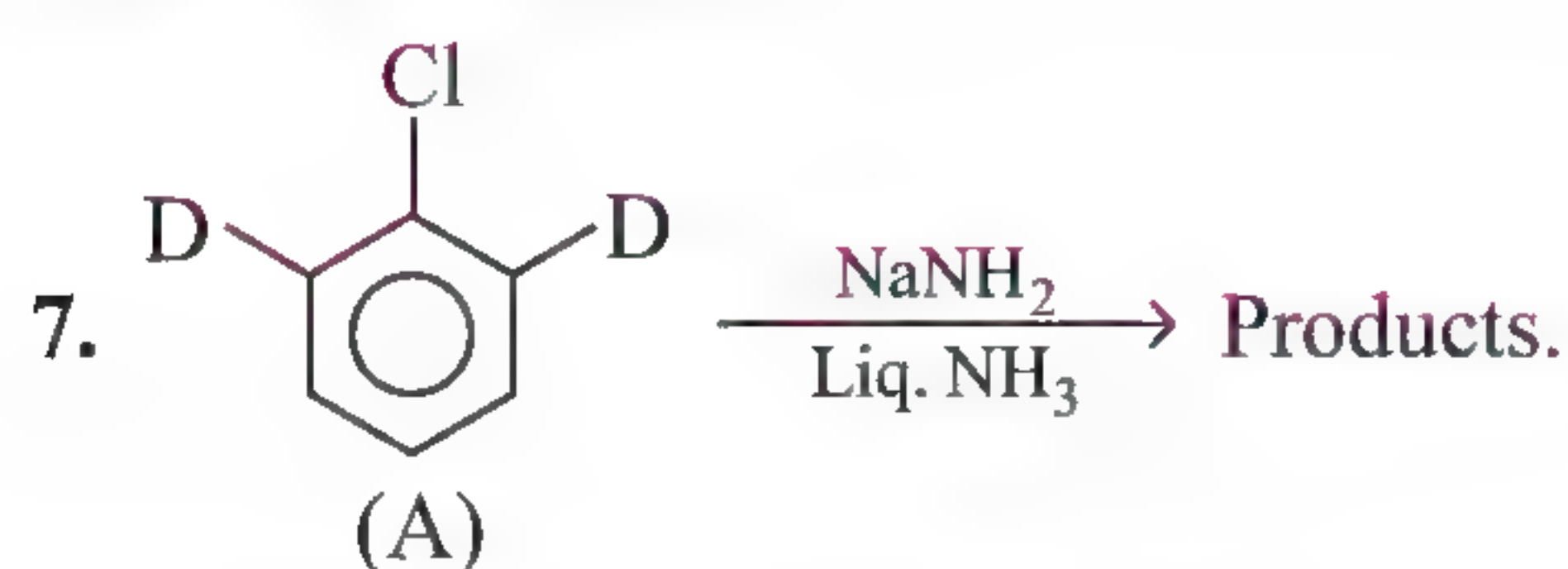
Which of the following statements are correct?

- (1) Phenol is formed via the formation of benzyne intermediate.
- (2) *p*-Phenyl phenol is also formed as a by-product.
- (3) Diphenylether is also formed as a by-product.
- (4) Biphenylene is also formed as a by-product.



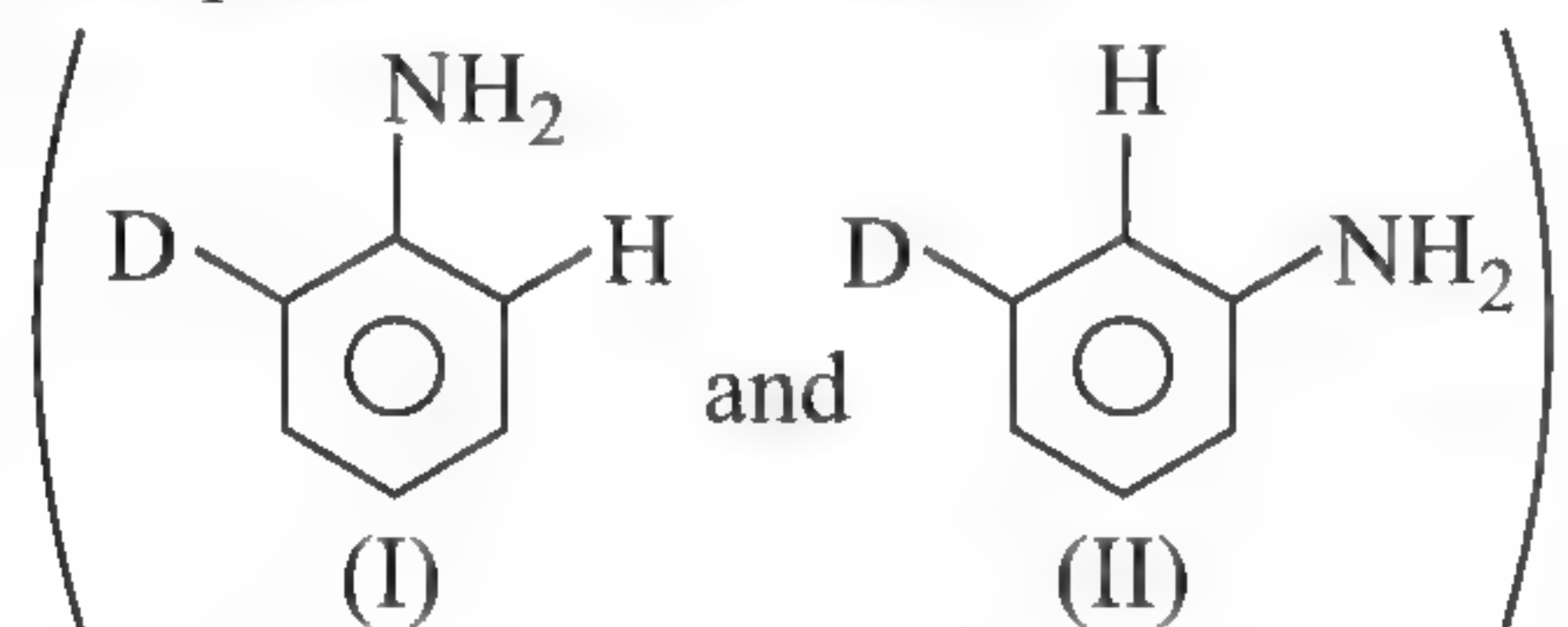
The products (I) and (II) are:





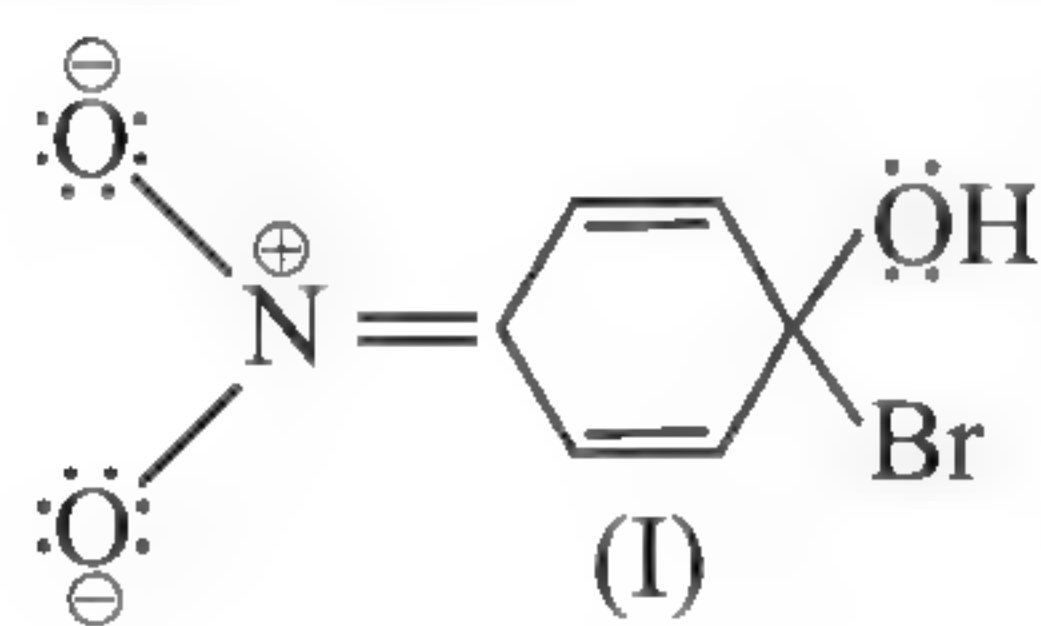
Which of the following statements are correct for the above reaction?

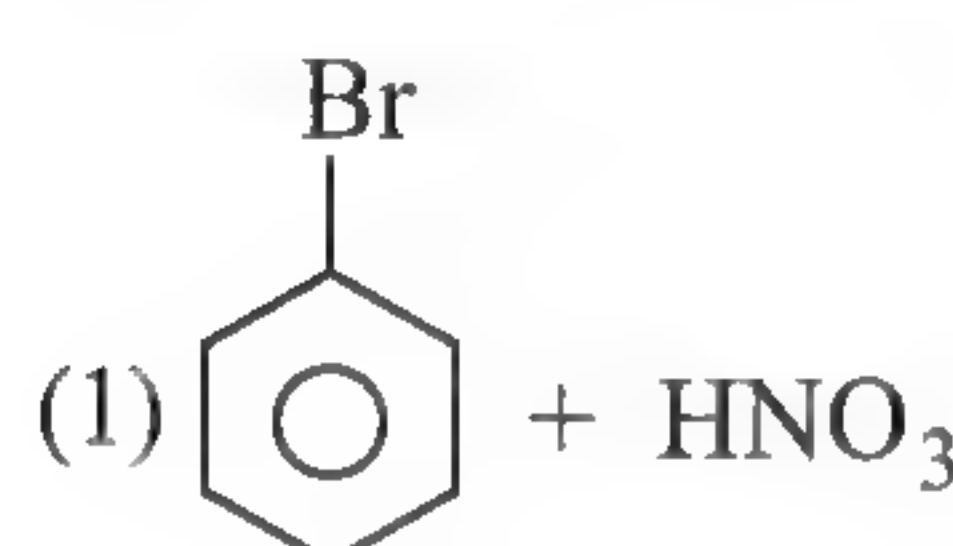
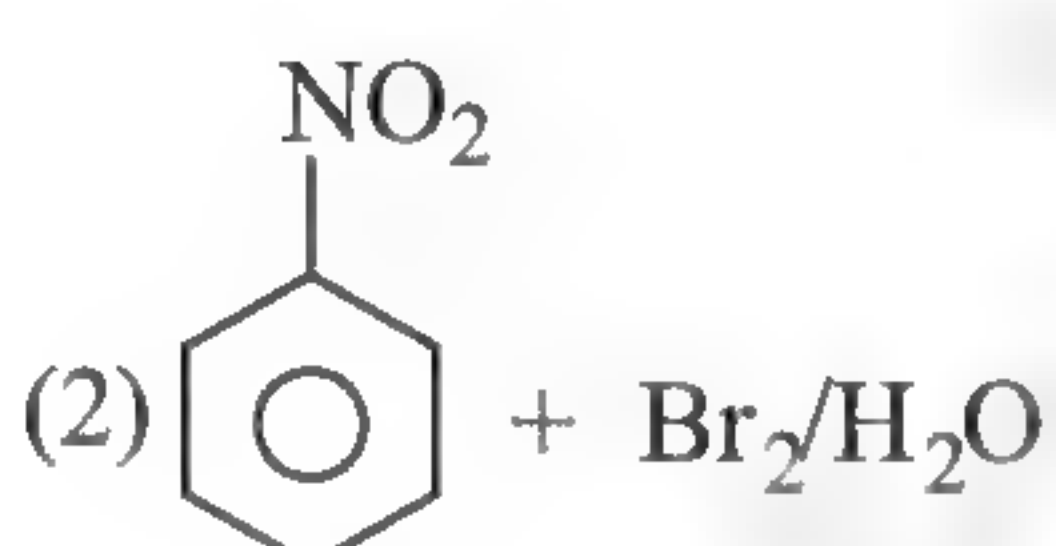
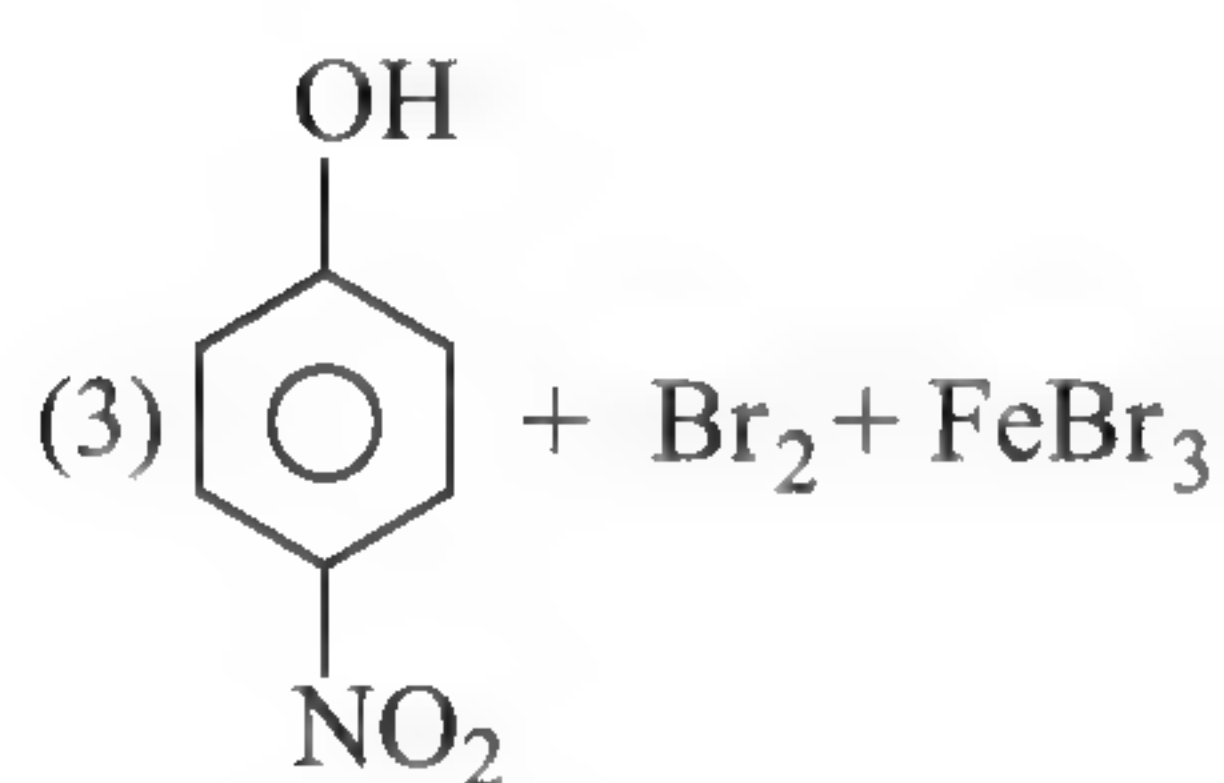
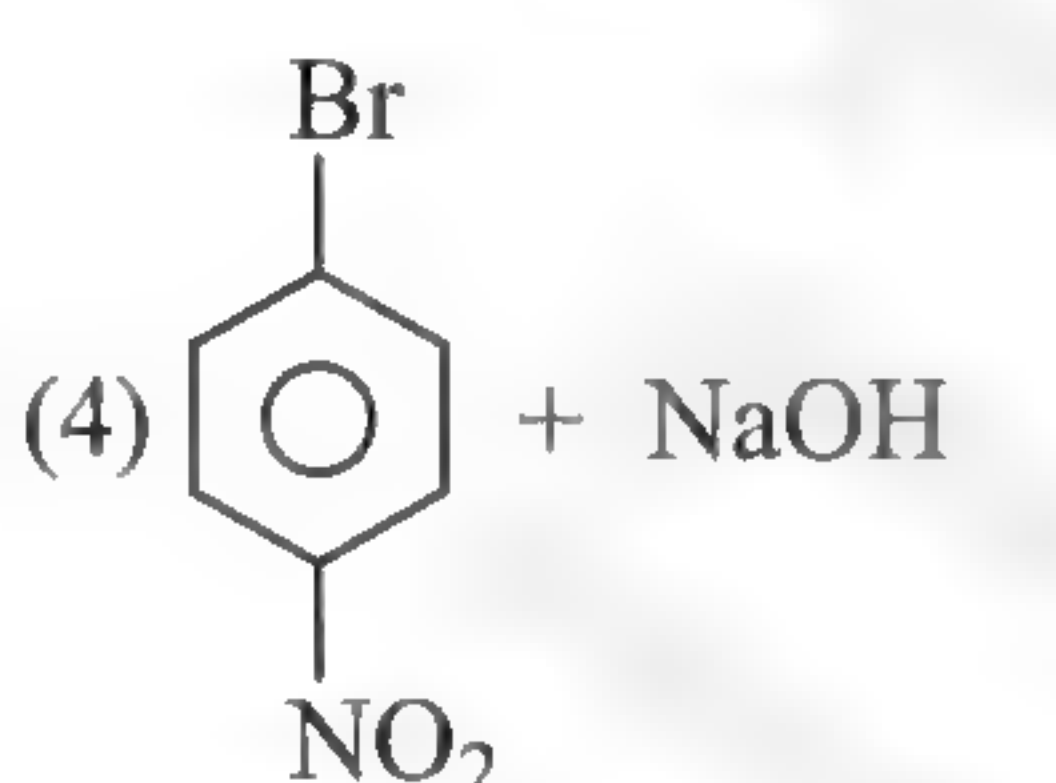
(1) The product is a mixture of



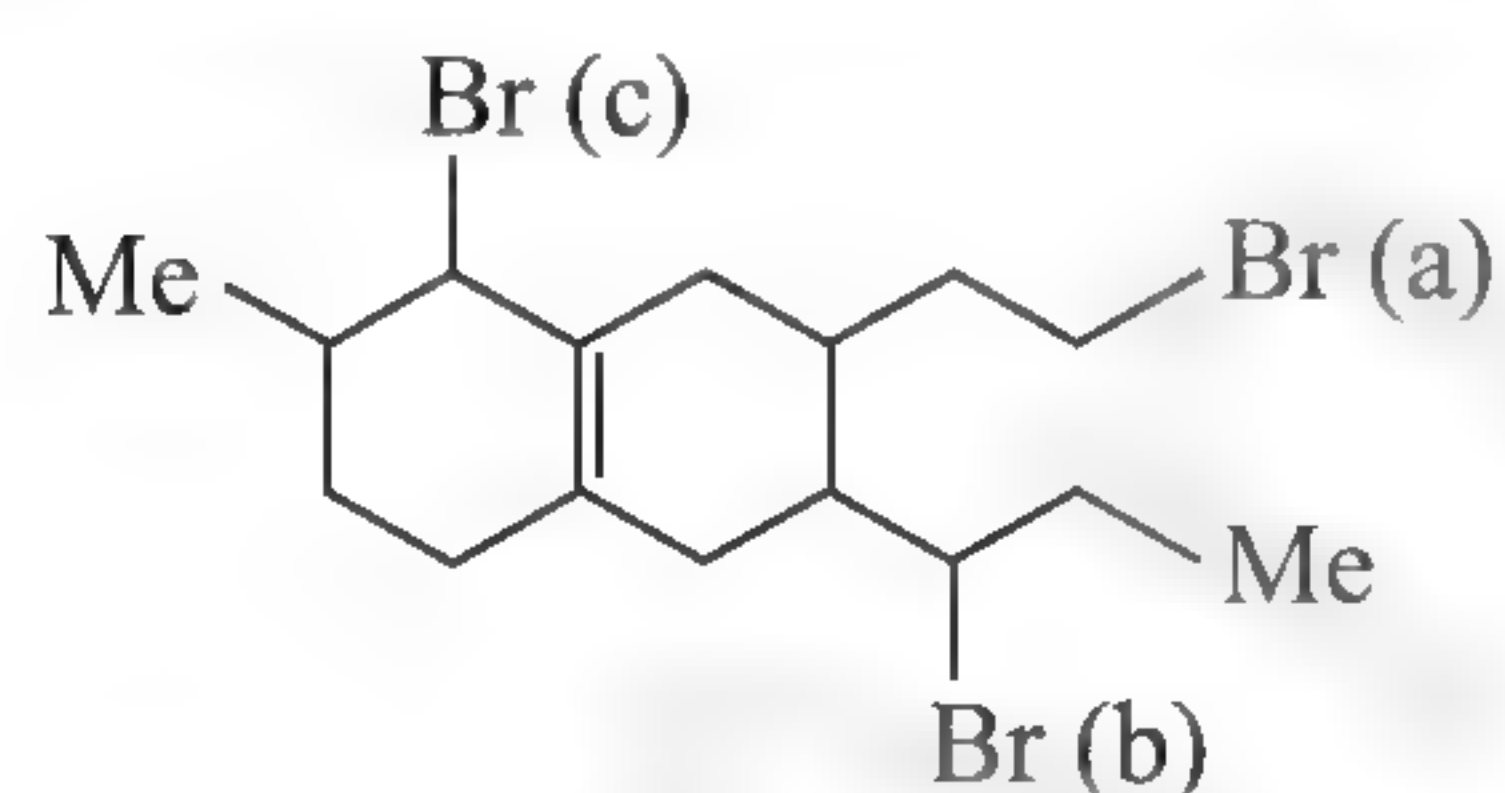
- (2) The product (II) is a cine-substitution product.
 (3) The reaction proceeds *via* benzene intermediate.
 (4) The reaction is ArSN (addition-elimination).

8. Which combination of reactants will not give species (I) shown as a reactive intermediate?



- (1)  + HNO₃ (2)  + Br₂/H₂O
 (3)  + Br₂ + FeBr₃ (4)  + NaOH

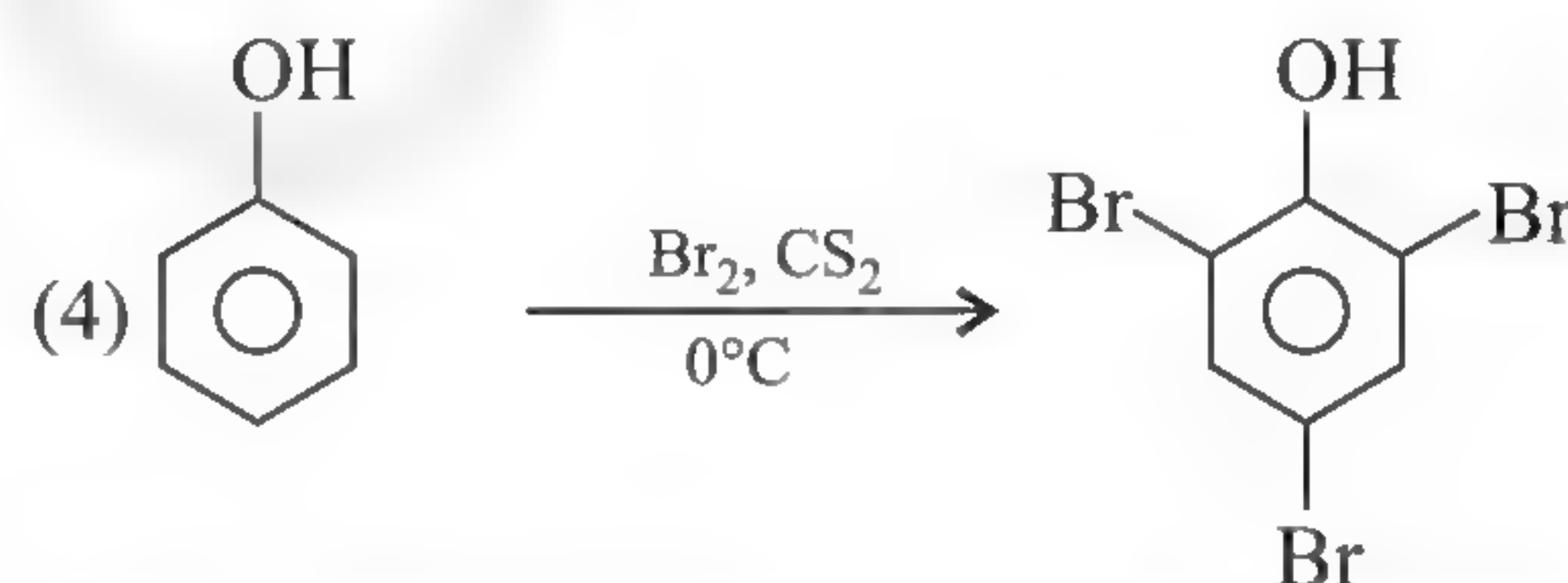
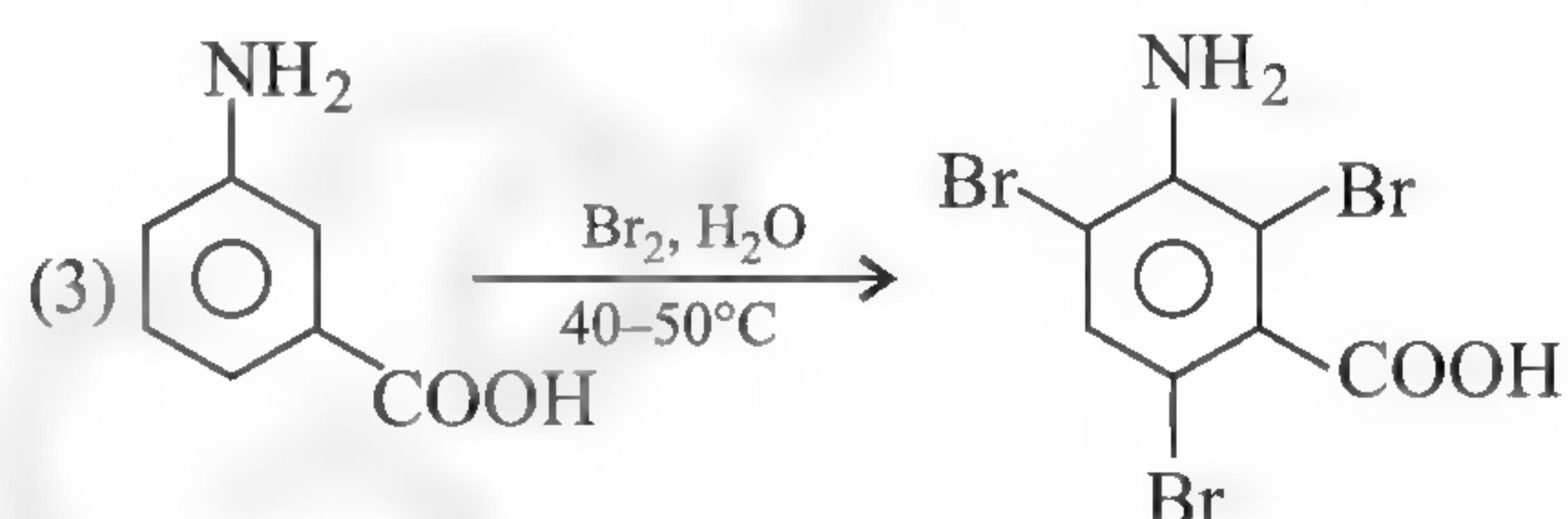
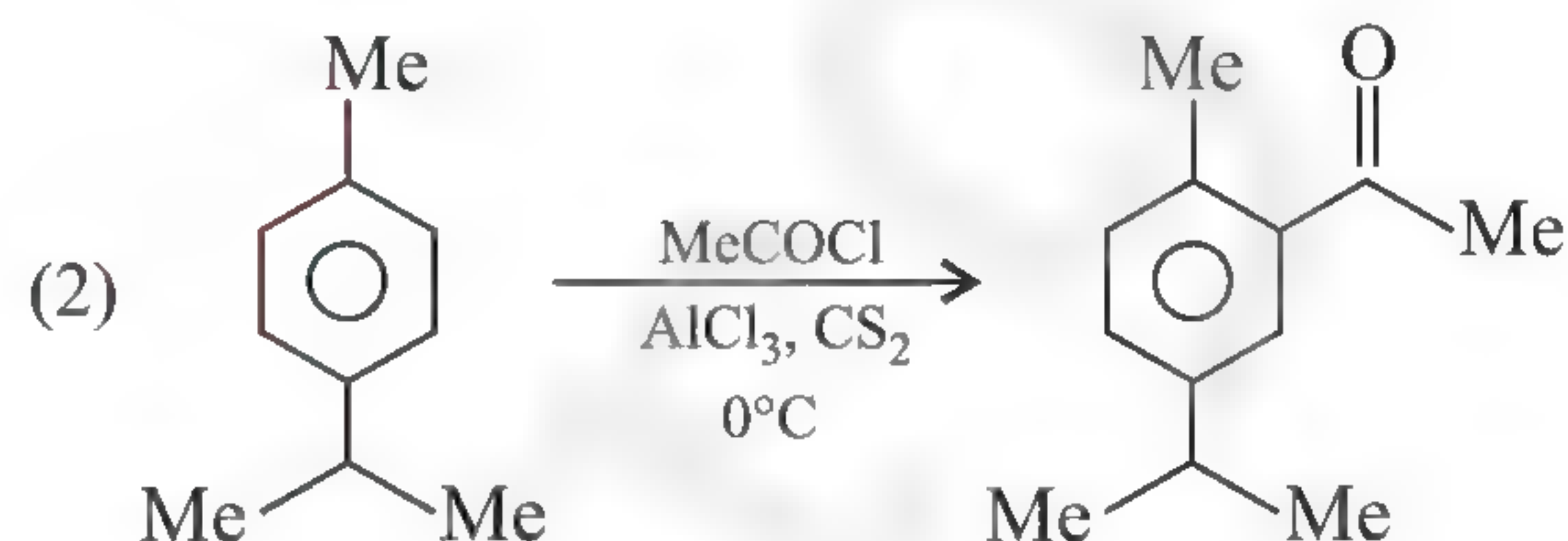
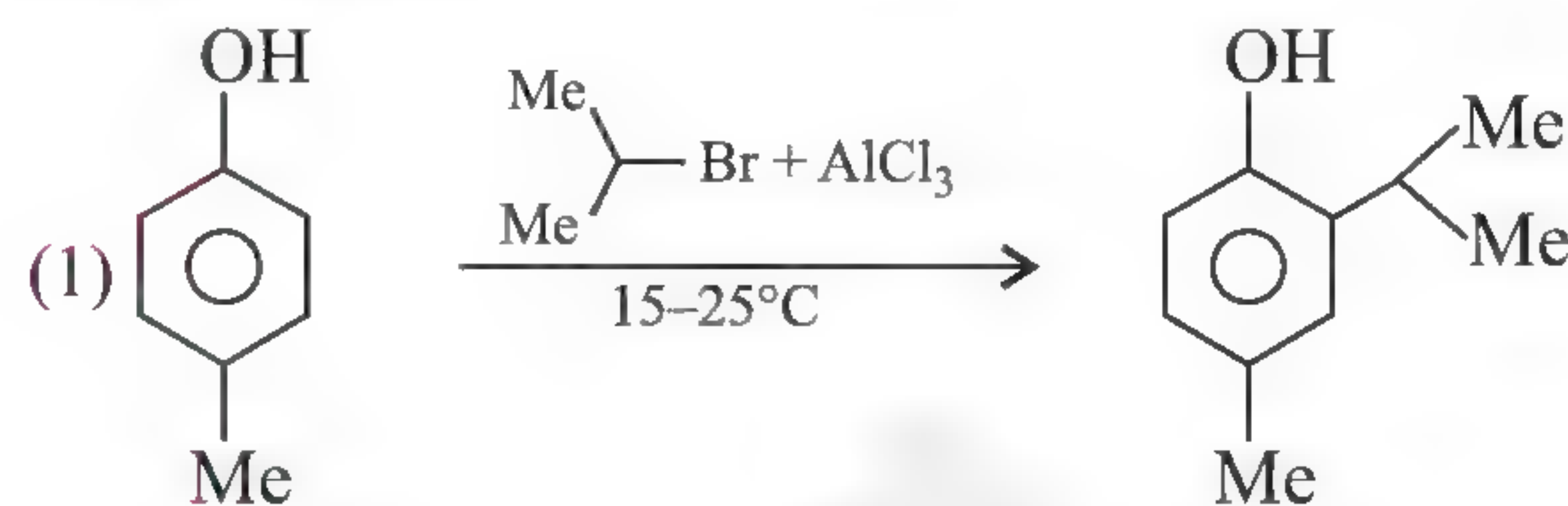
9. Consider the following compound:



Which of the following statements are correct?

- (1) Loss of Br (a) atom in dehydrobromination reaction results in the formation of the most reactive double bond towards hydrogenation reaction.
 (2) Removal of Br (c) atom results in the formation of the most stable carbocation.
 (3) The above compound contains five asymmetric C atoms.
 (4) The above compound does not show geometrical isomers.

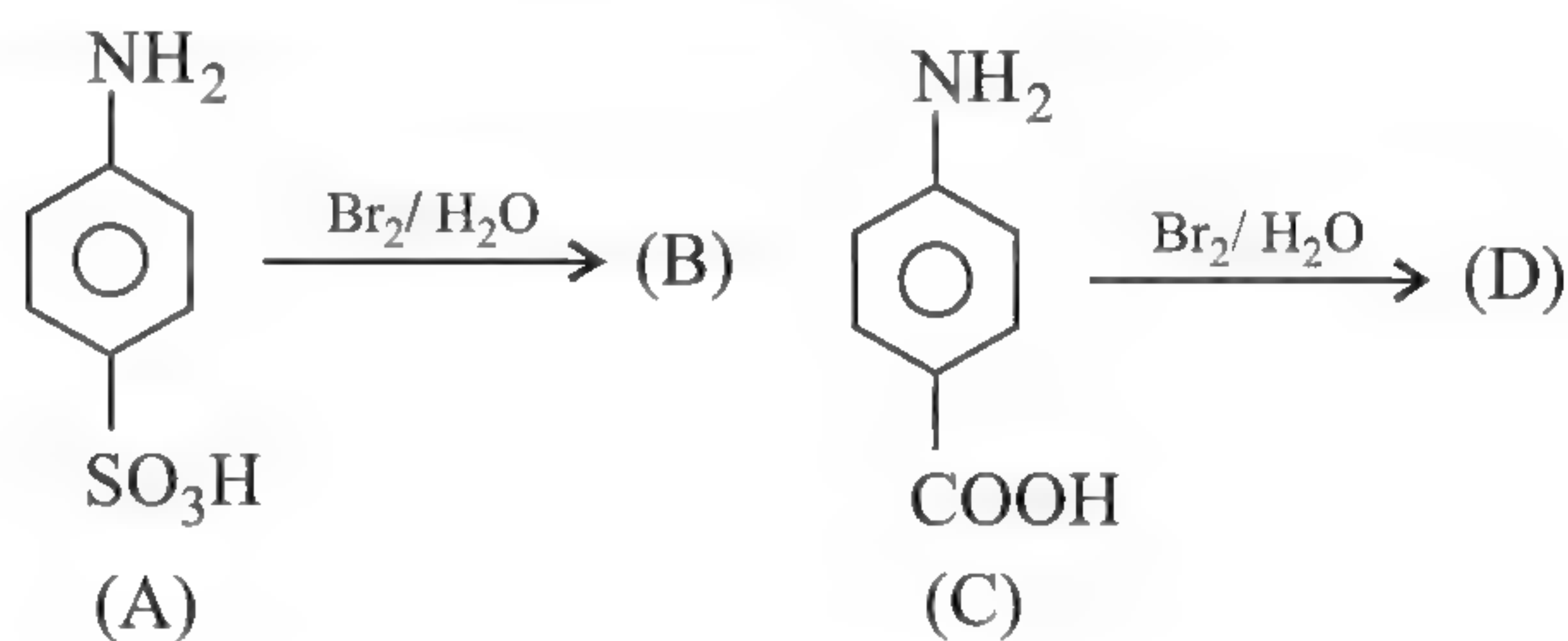
10. In which of the following reactions is the correct major product formed is/are



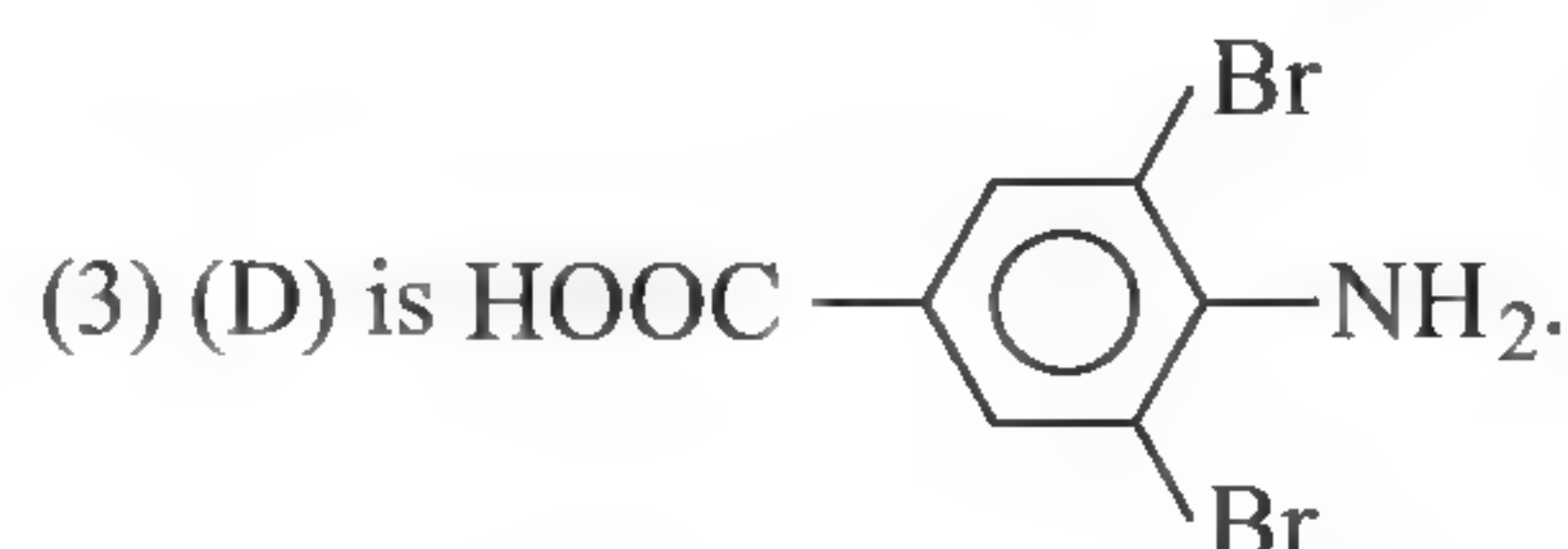
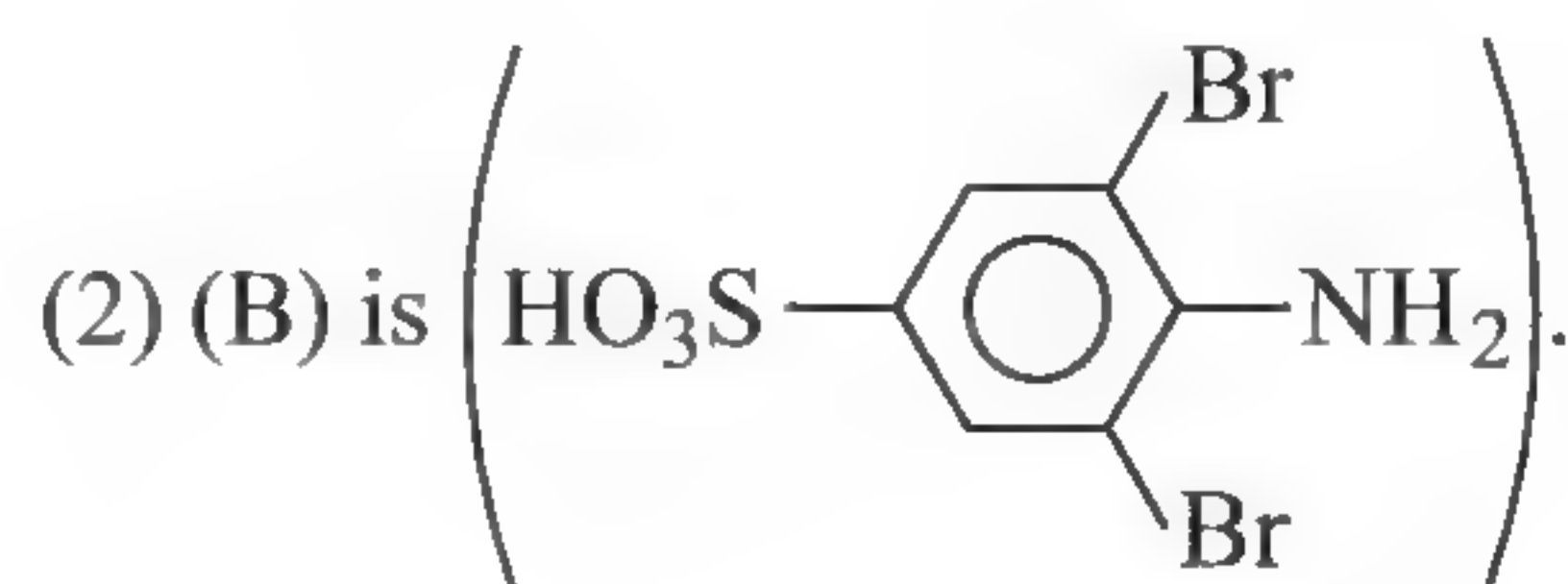
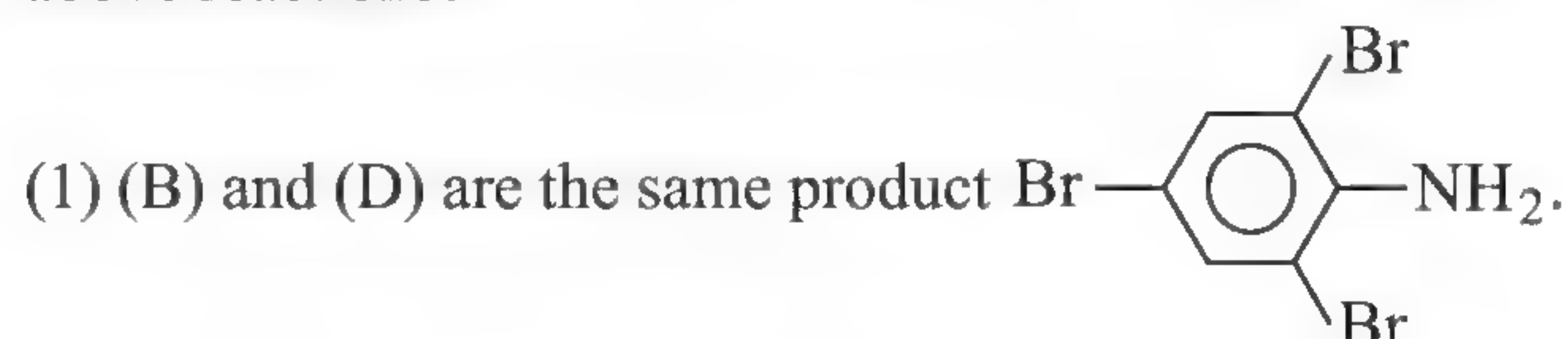
11. Which of the following side chain reactions can be used to reduce the activity of strongly activating groups such as (–OH) or (–NH₂)?

- (1) Benzoylation (2) Acetylation
 (3) Tosylation (4) Sulphonation

12. In the following reactions:



Which of the following statements are correct about the above reactions?



(4) The above reaction is called ipso substitution.

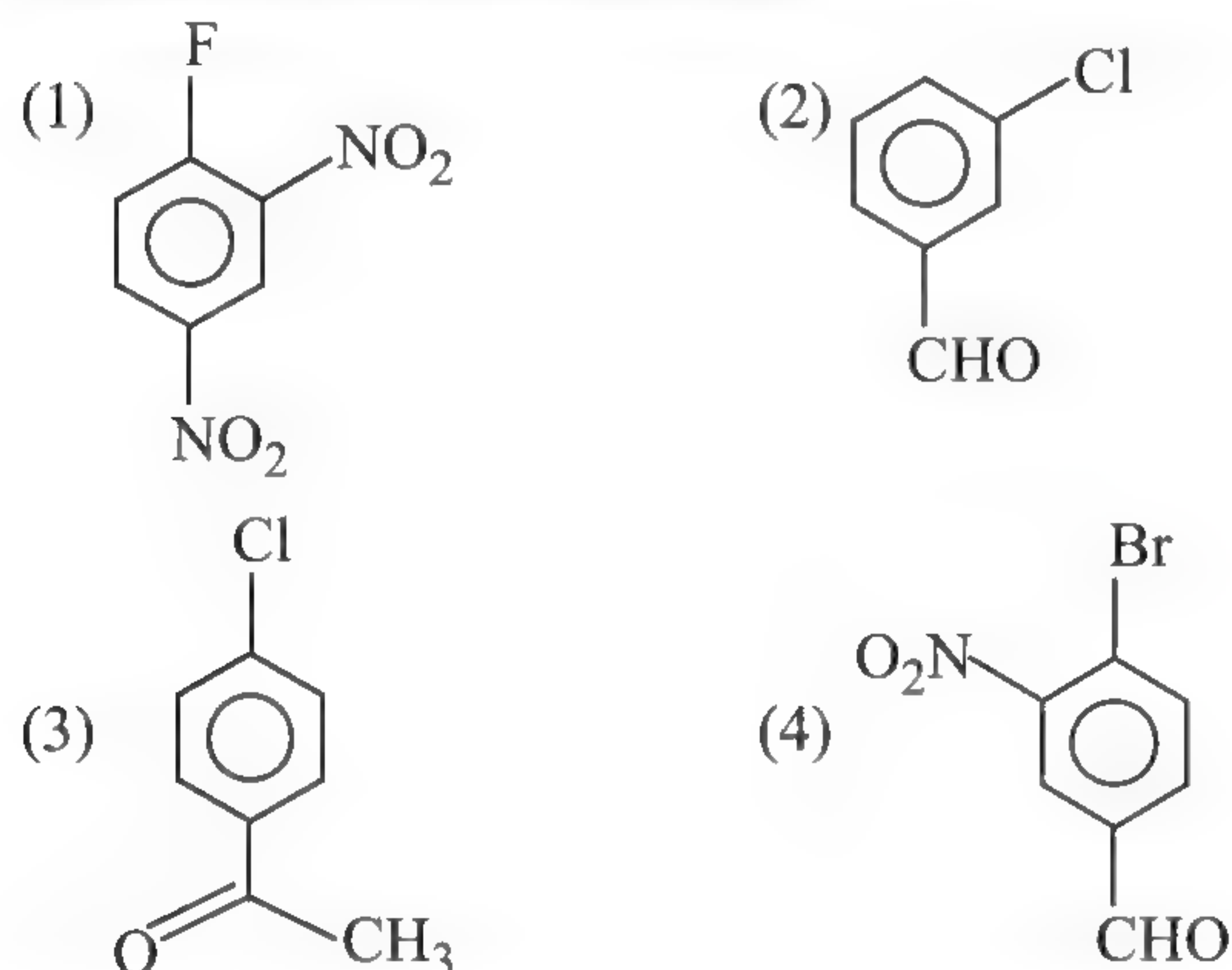
13. Which are the sources of phenol?

- (1) Cumene
- (2) Hydrolysis of benzene diazonium salt
- (3) Middle oil of coal tar distillation
- (4) Reaction of diazonium salt with H_3PO_2

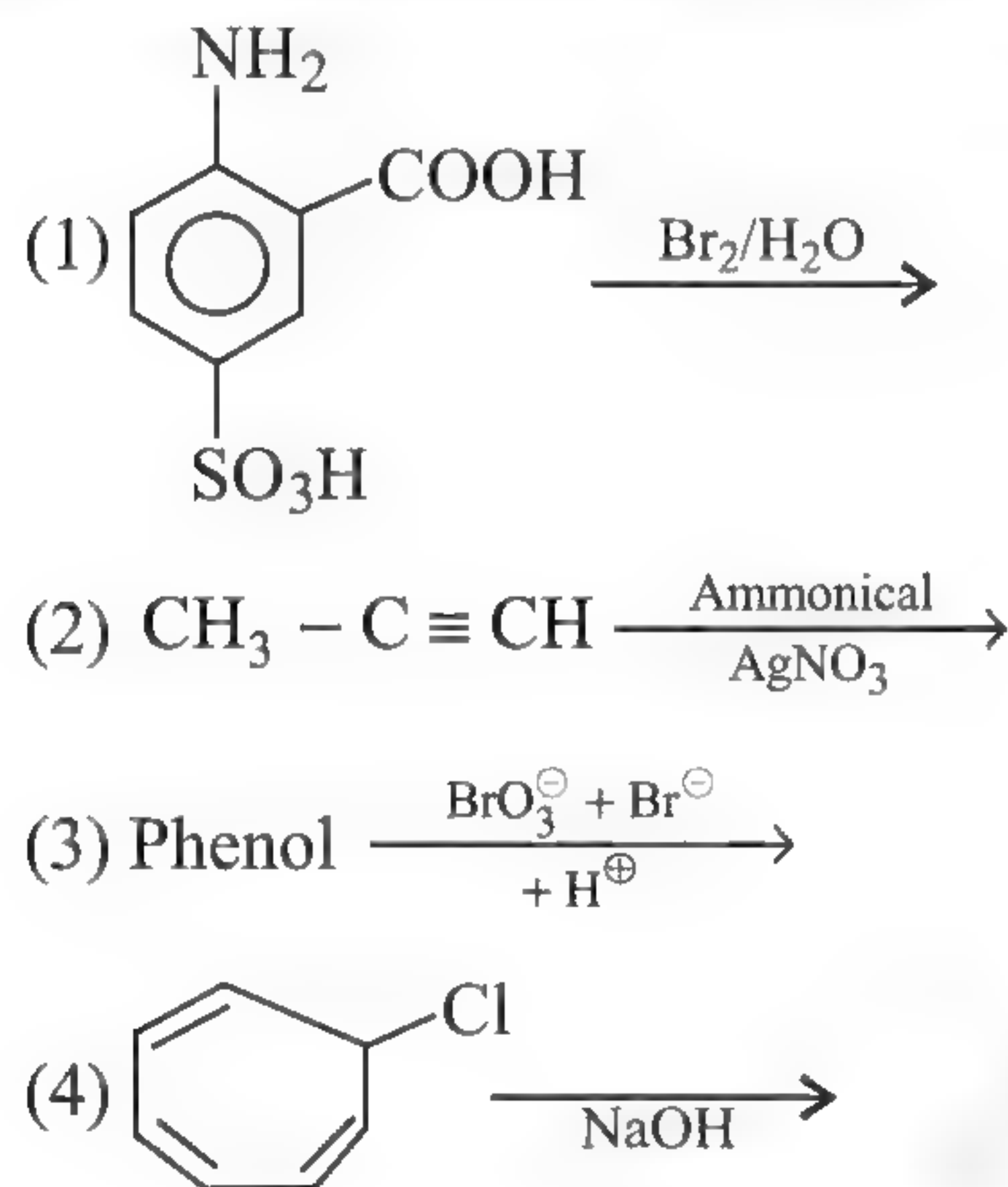
14. When benzene sulphonic acid and *p*-nitrophenol are treated with NaHCO_3 , the gases released, respectively, are:

- (1) SO_2 , NO_2
- (2) SO_2 , NO
- (3) SO_2 , CO_2
- (4) CO_2 , CO_2

15. Identify the compounds that will undergo nucleophilic aromatic substitution reaction:



16. Which of the reaction(s) will produce white precipitate?



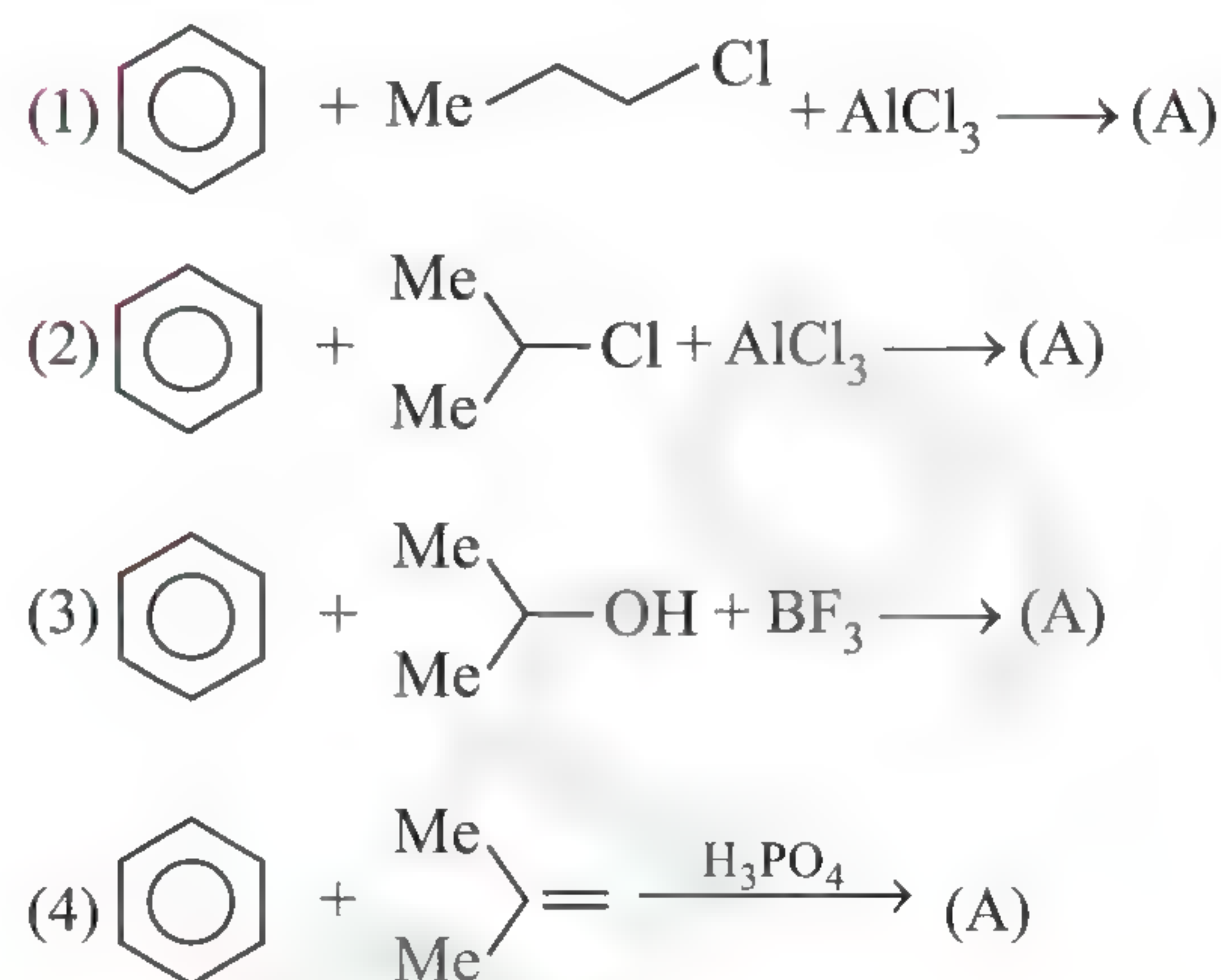
17. Select the **incorrect** statement(s).

- (1) Freon-23 is $\text{C}_2\text{F}_4\text{Cl}_2$.
- (2) Three types of Freon-22 exists.
- (3) Freon-12 is prepared by reacting CCl_4 with SbF_5 .
- (4) Freons are used as refrigerants.

18. Select the **incorrect** statement(s).

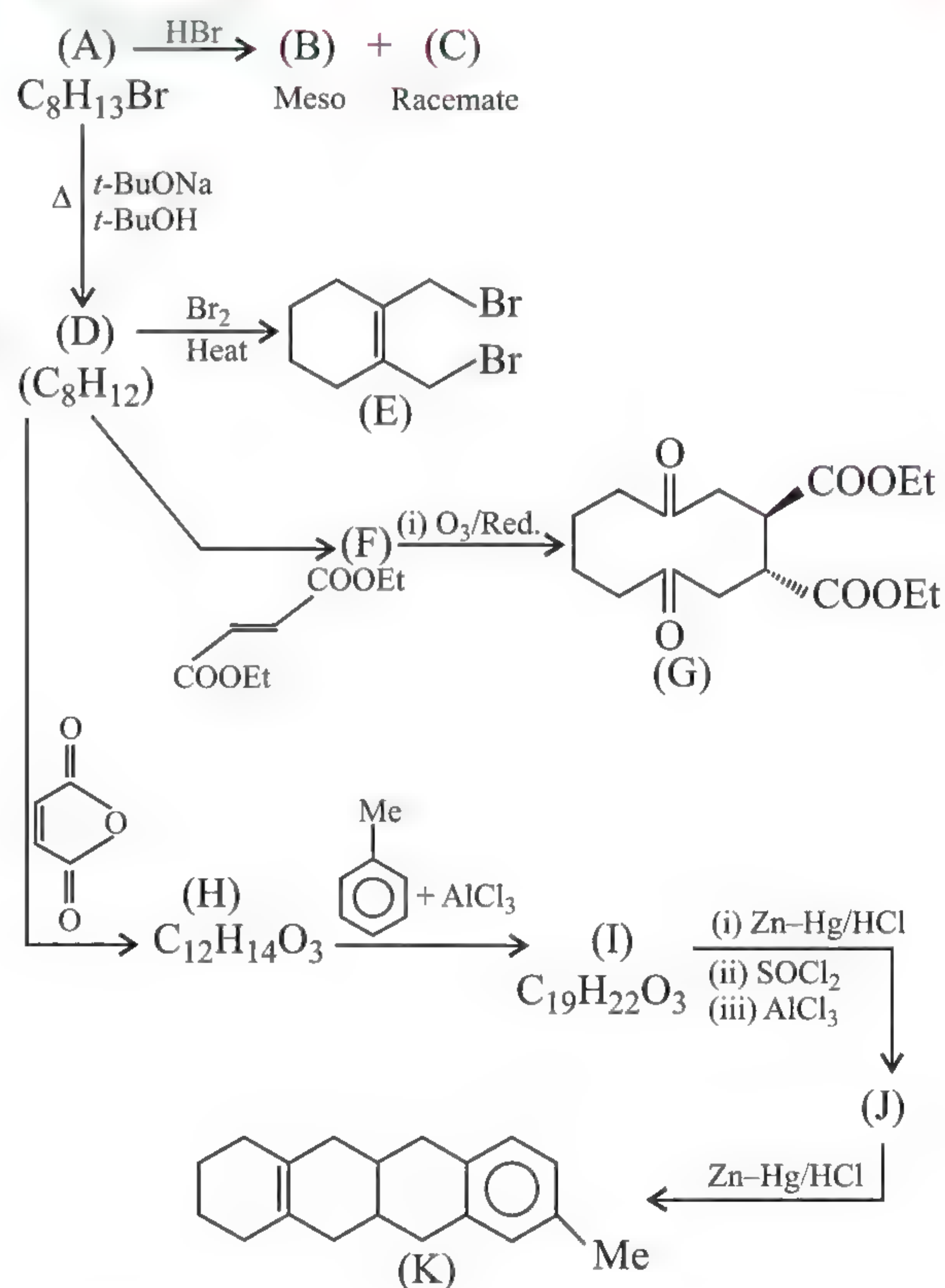
- (1) Perchloro benzene is prepared by chlorination of benzene in presence of light.
- (2) Perfluoro octane is prepared by controlled fluorination of octene in presence of CoF_2 catalyst.
- (3) *p, p'*-Dichlorodiphenyl trichloroethane is prepared from chlorobenzene and ethanal.
- (4) C_7F_{16} is used in carbon monoxide poisoning.

19. Which of the following are the best methods for the preparation of cumene (A)?

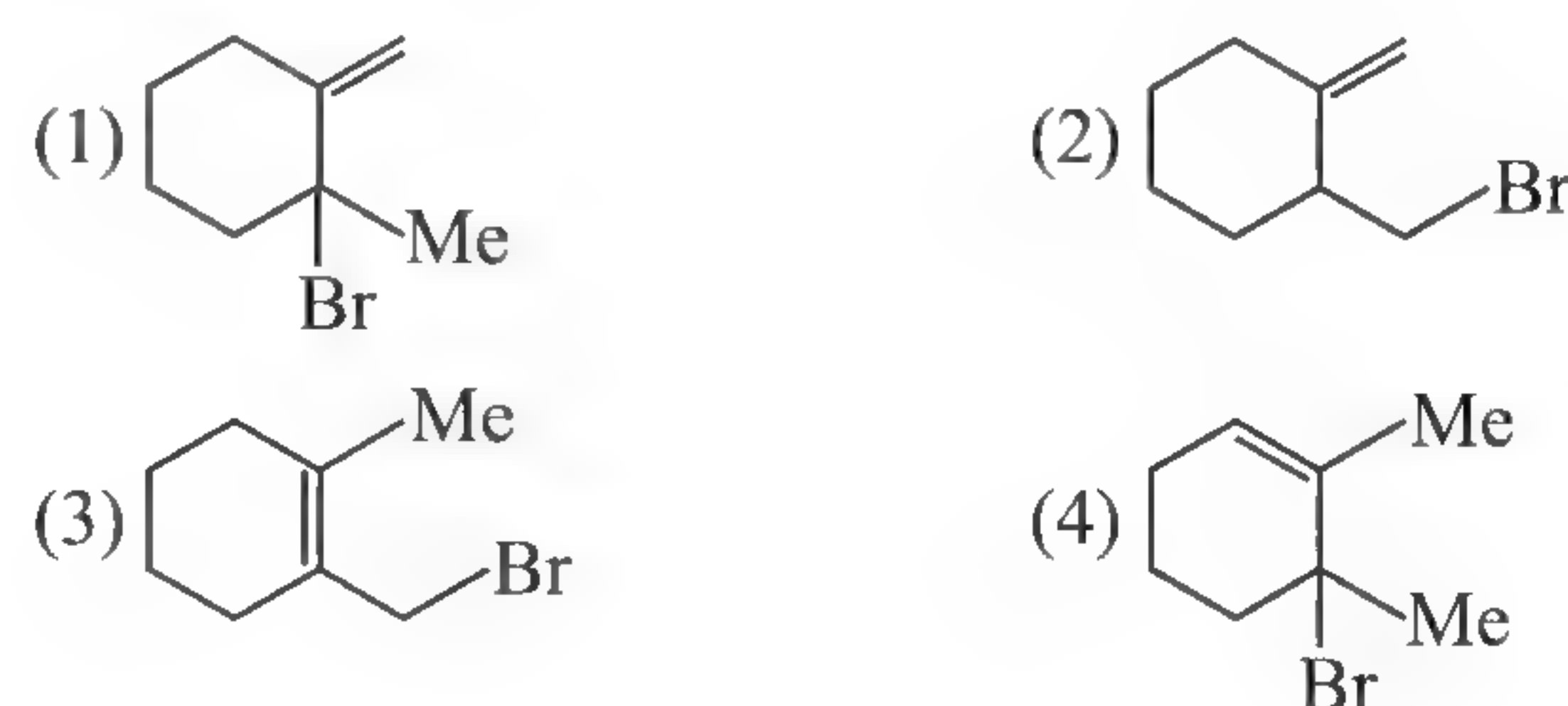


Linked Comprehension Type

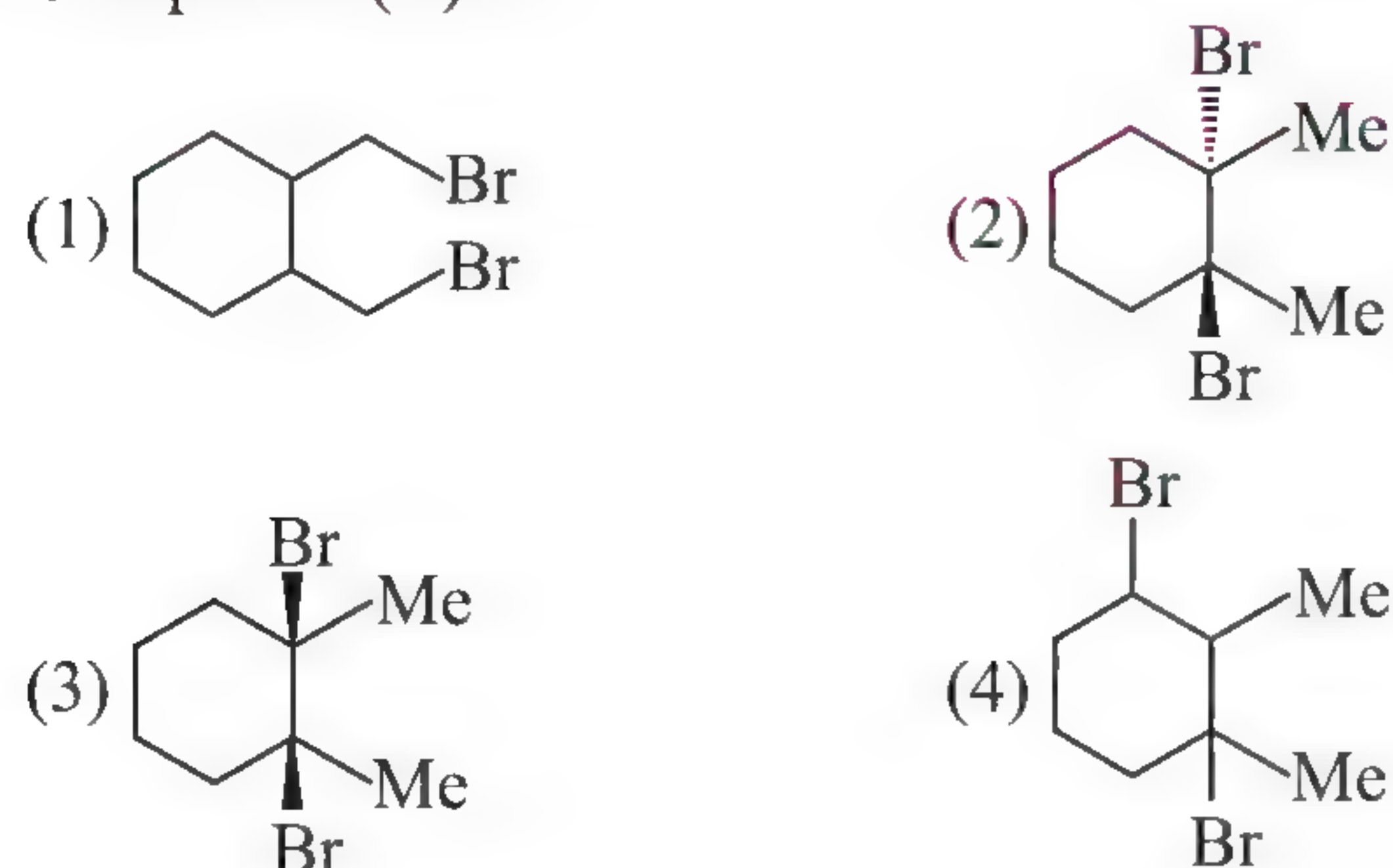
Paragraph 1



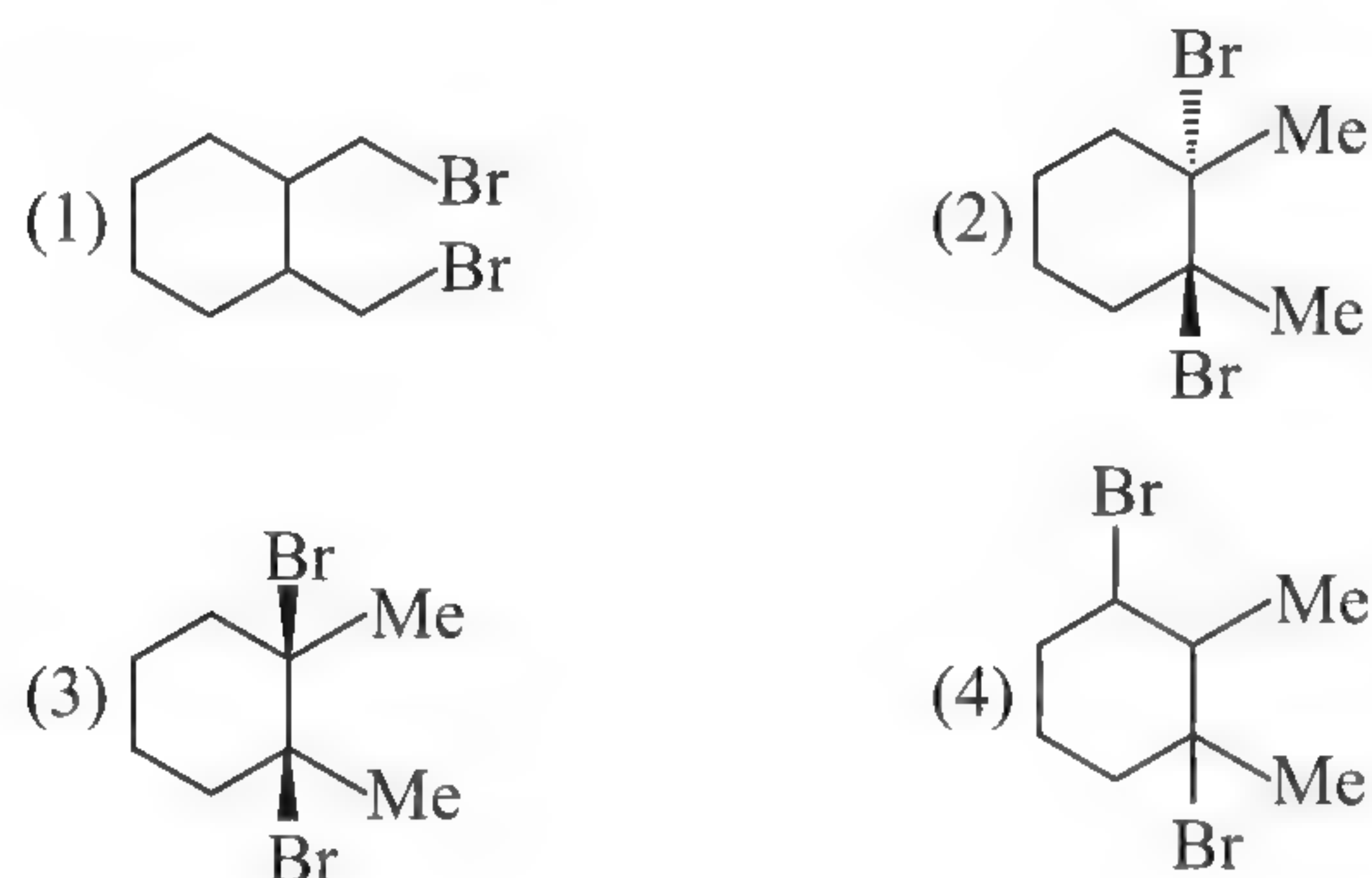
1. Compound (A) is:



2. Compound (B) is:



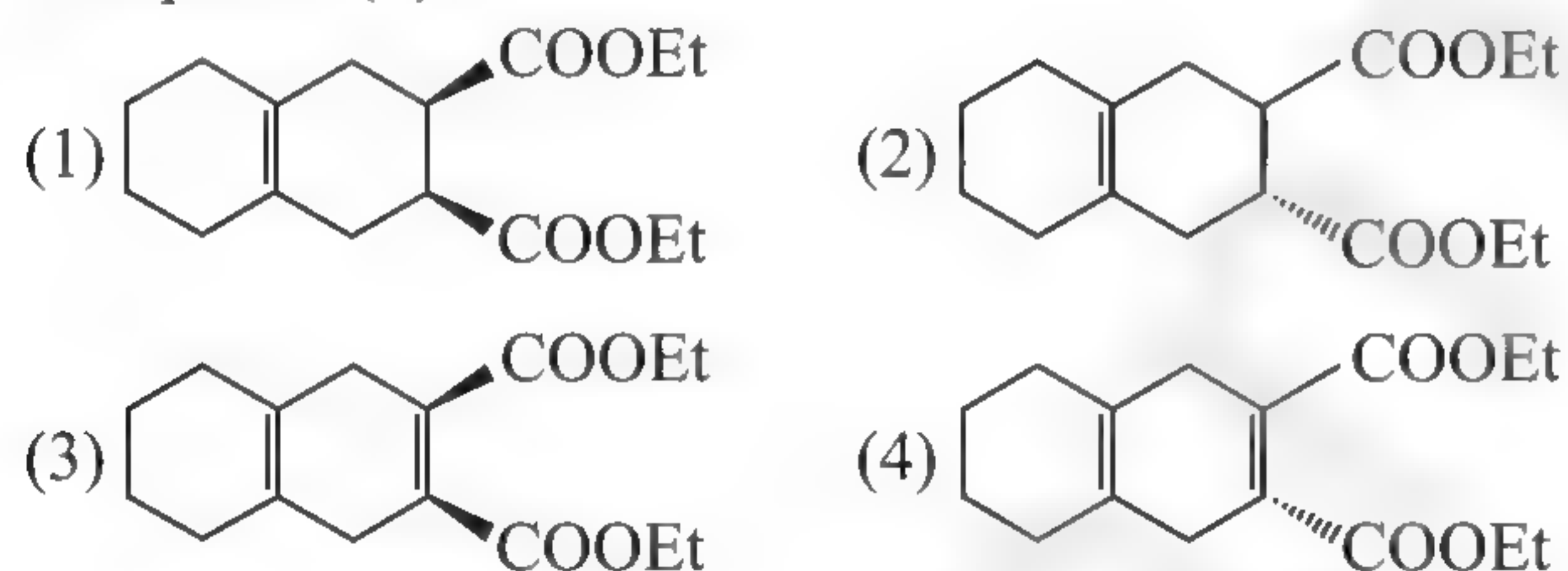
3. Compound (C) is:



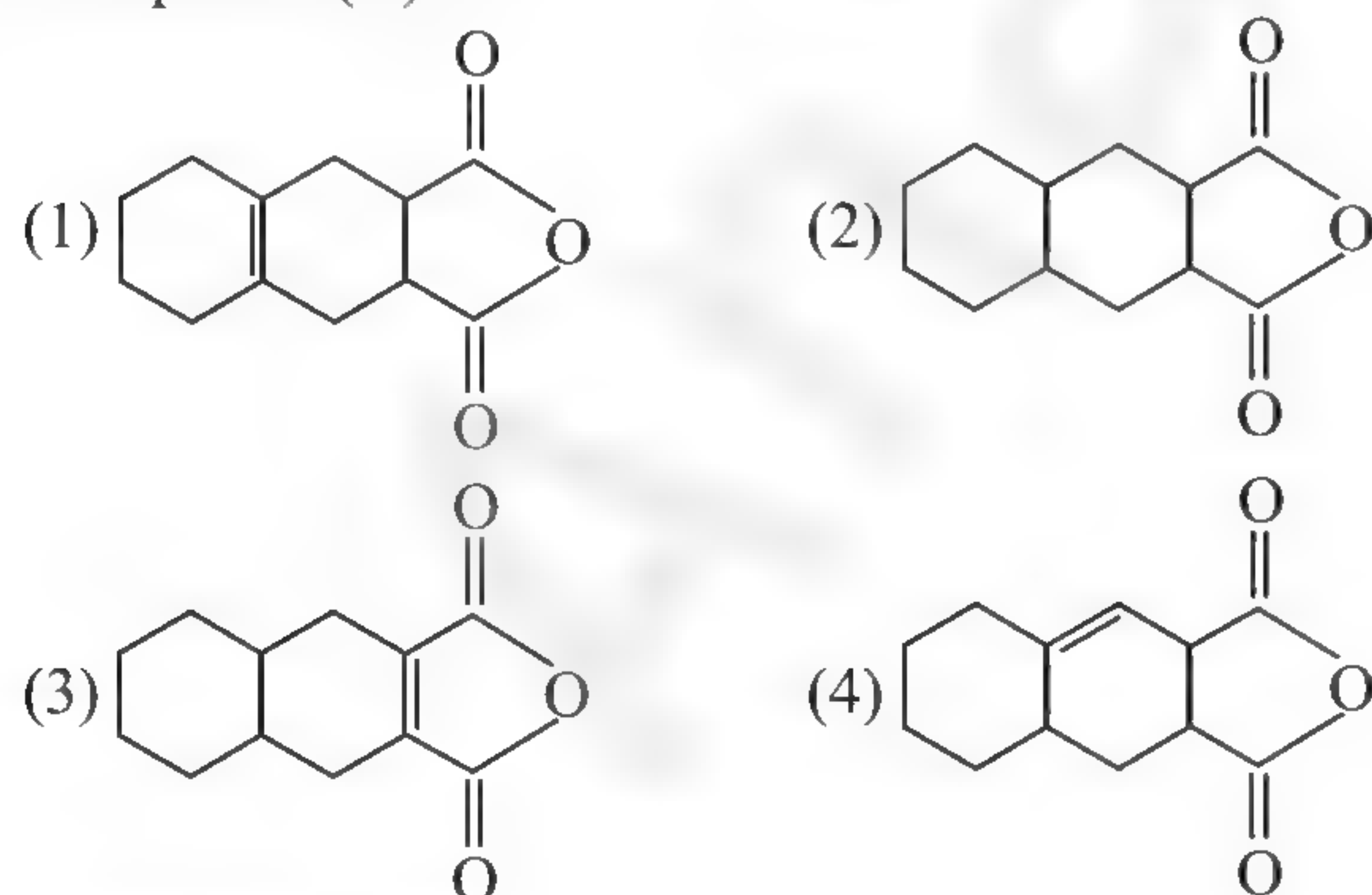
4. Compound (D) is:



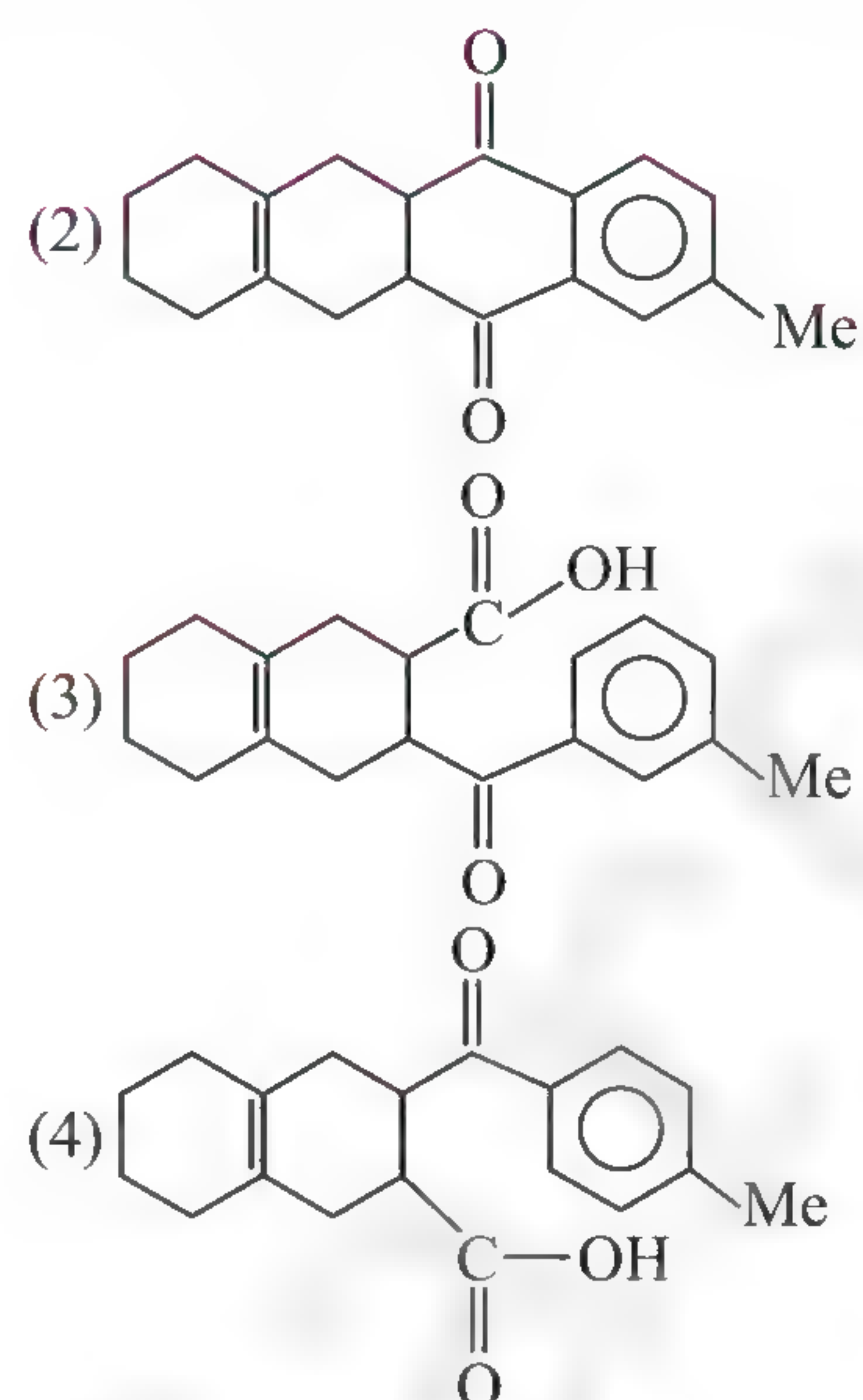
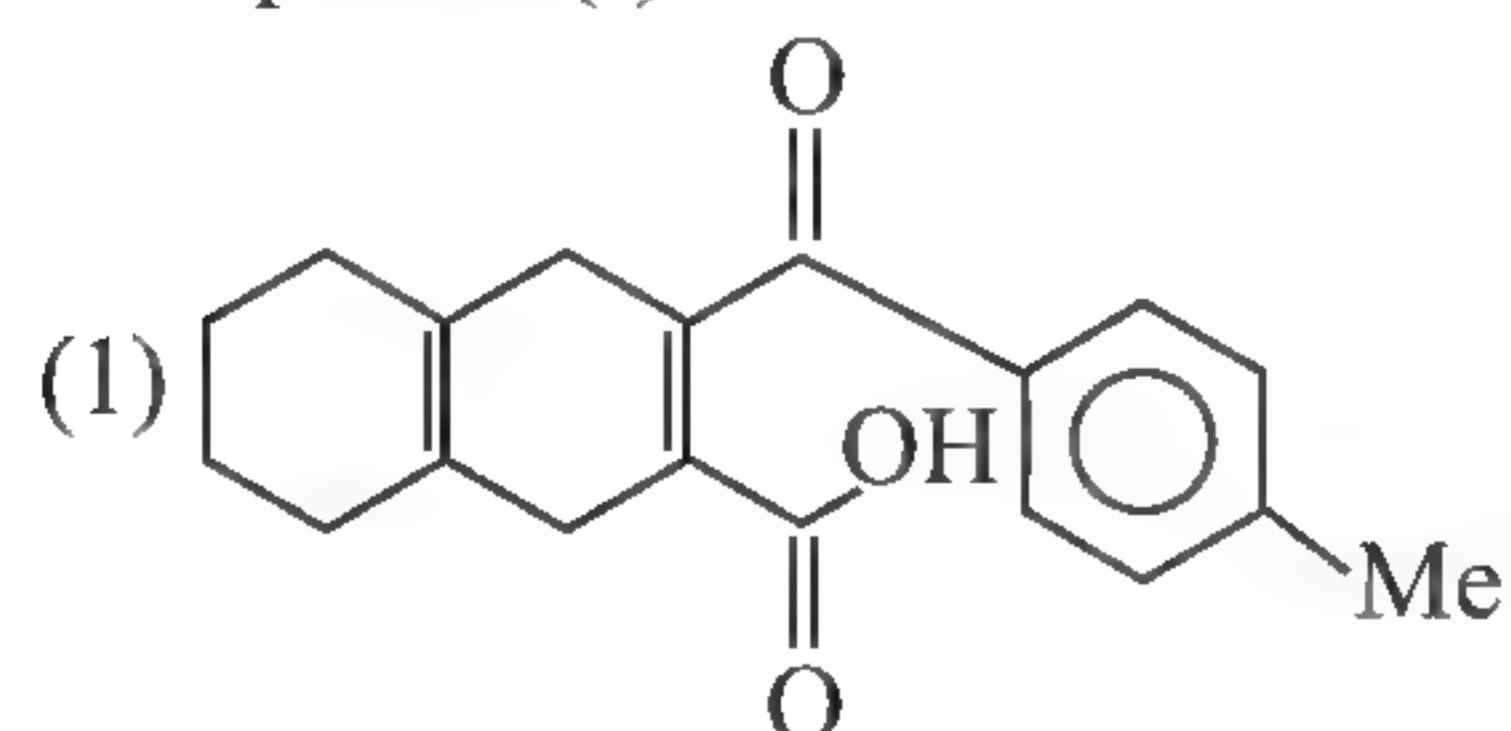
5. Compound (F) is:



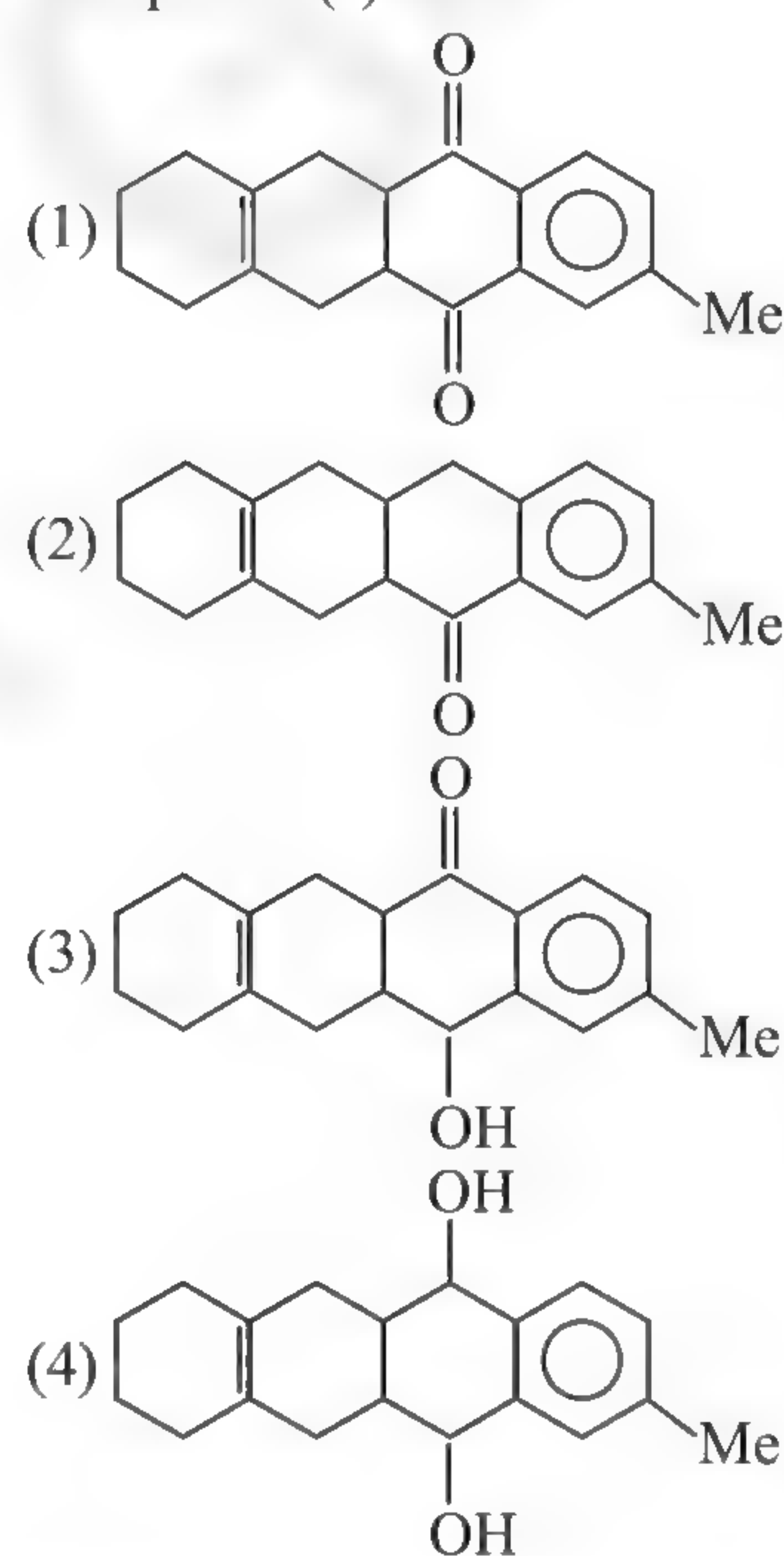
6. Compound (H) is:



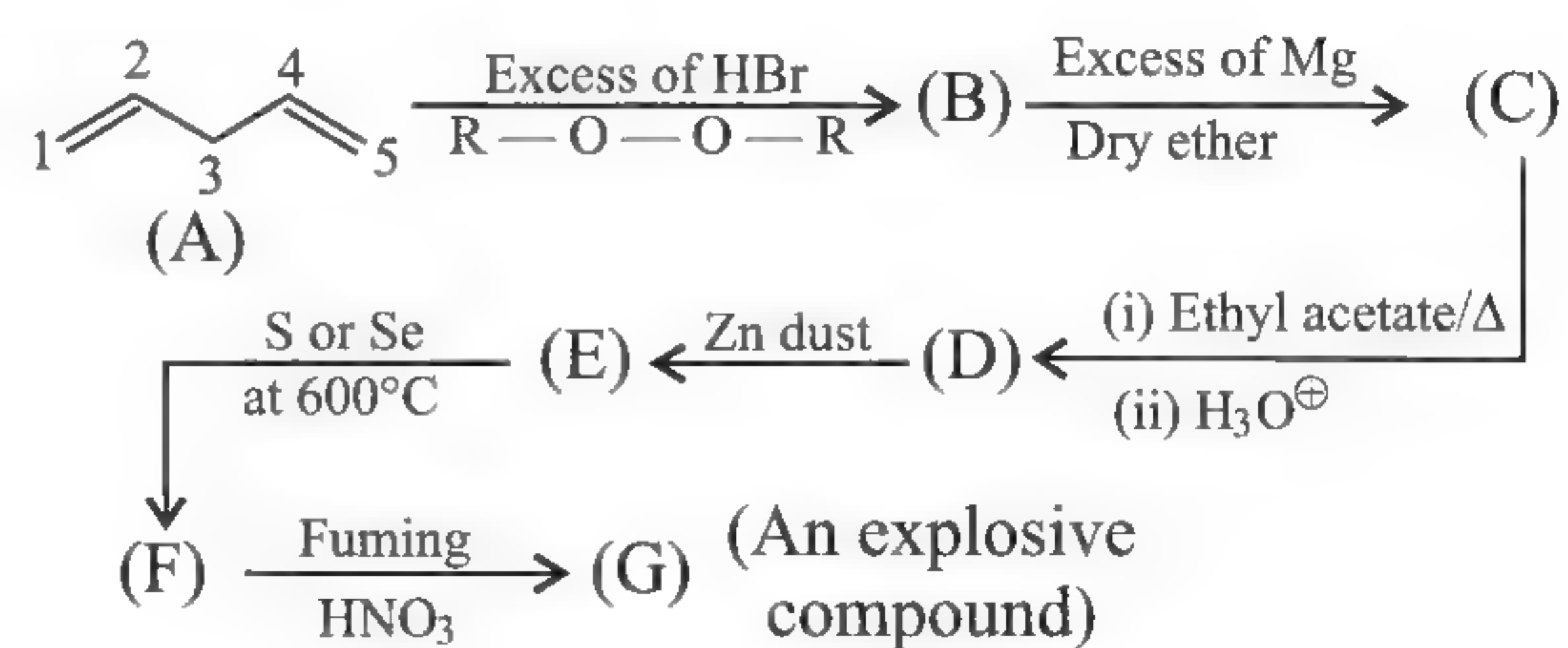
7. Compound (I) is:



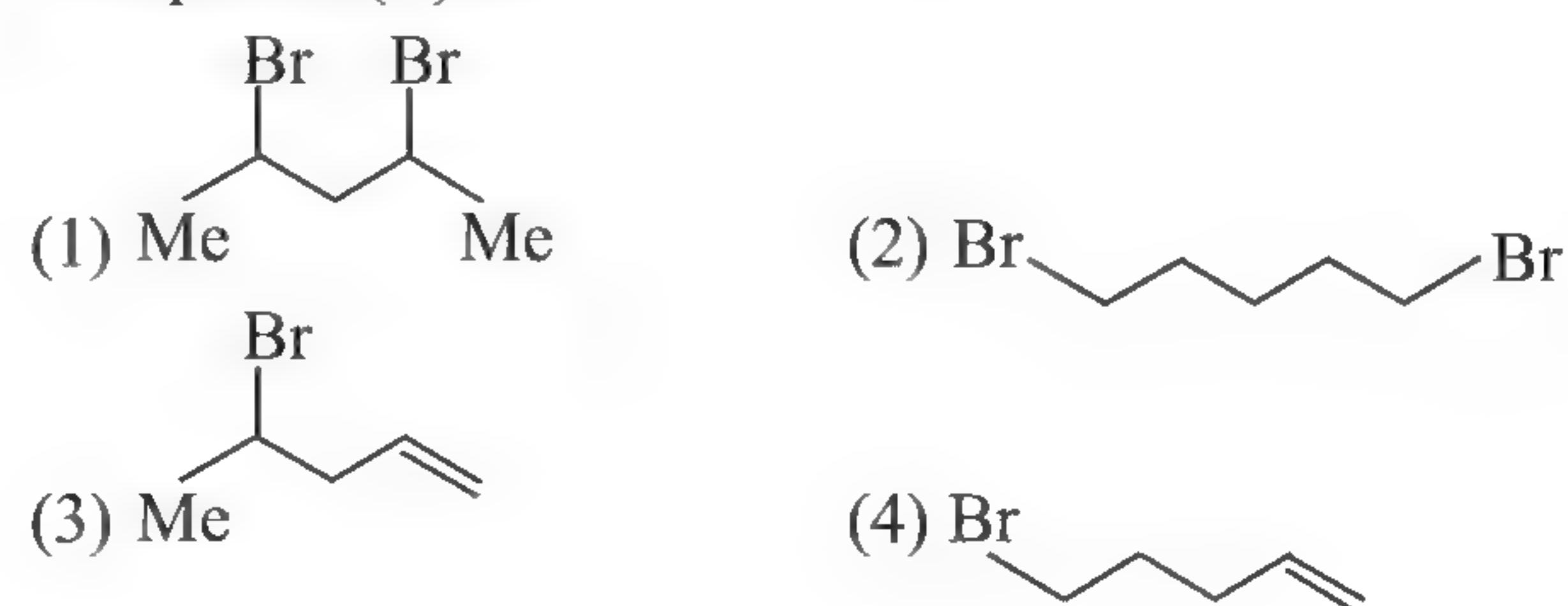
8. Compound (J) is:



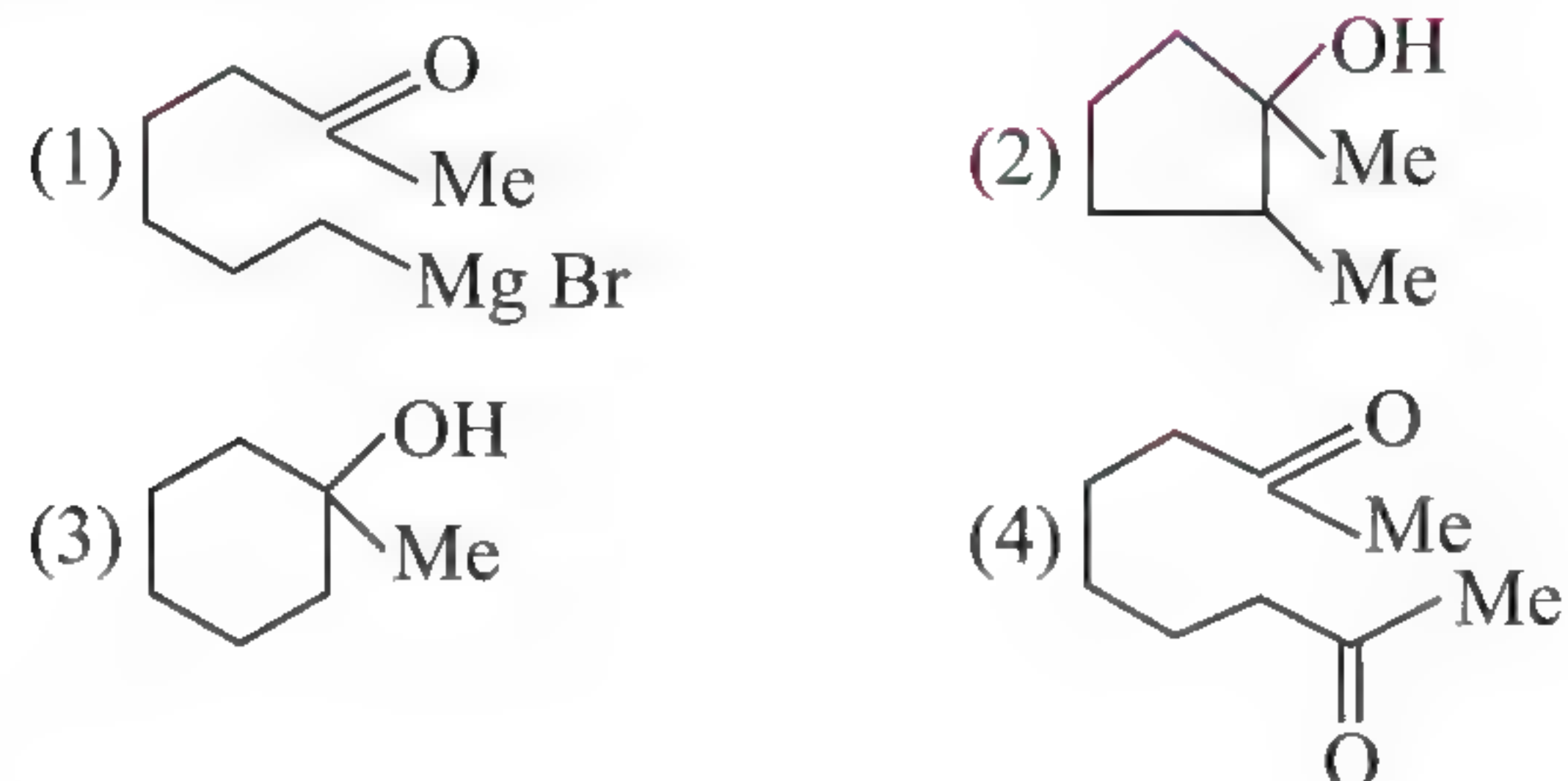
Paragraph 2



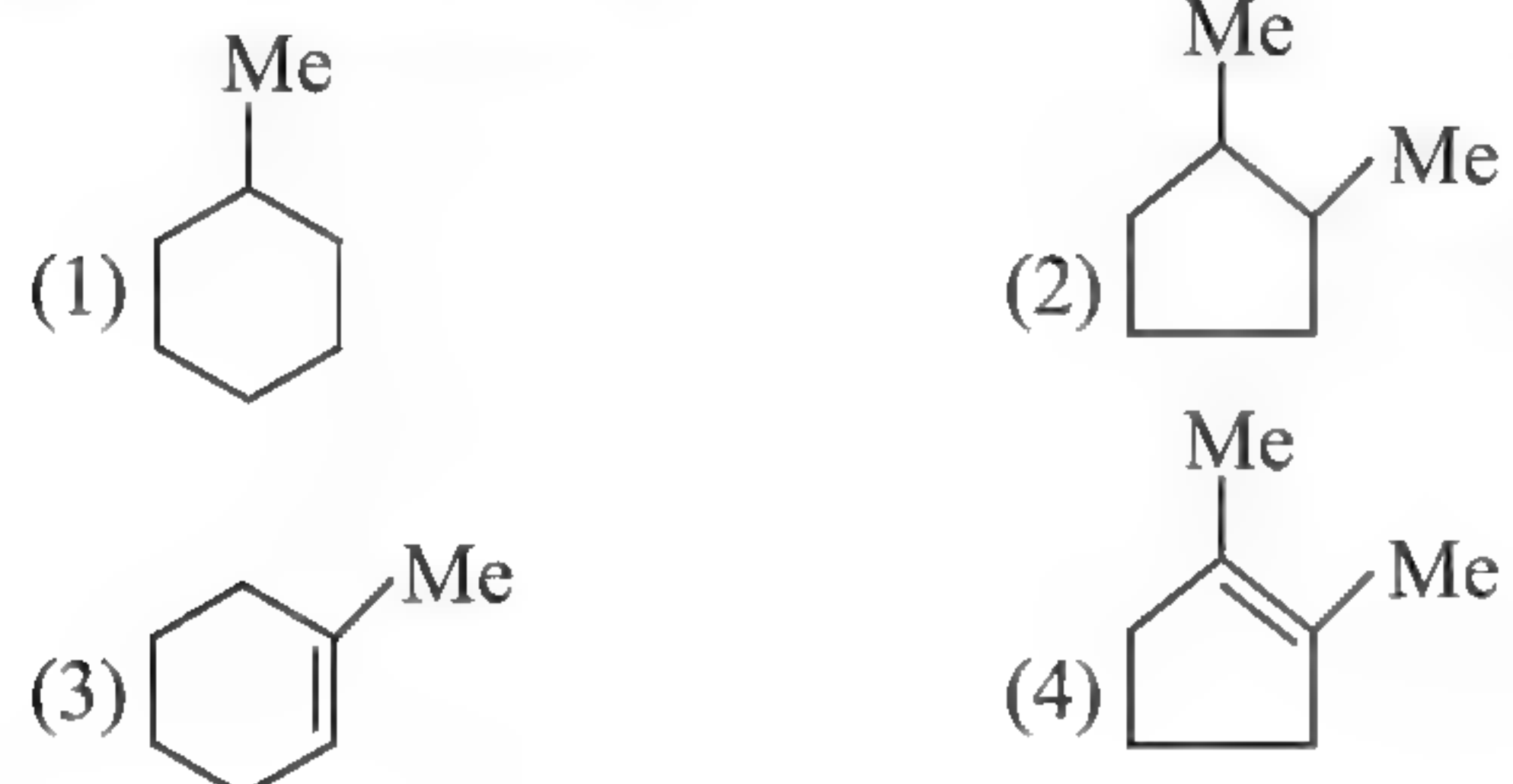
9. Compound (B) is:



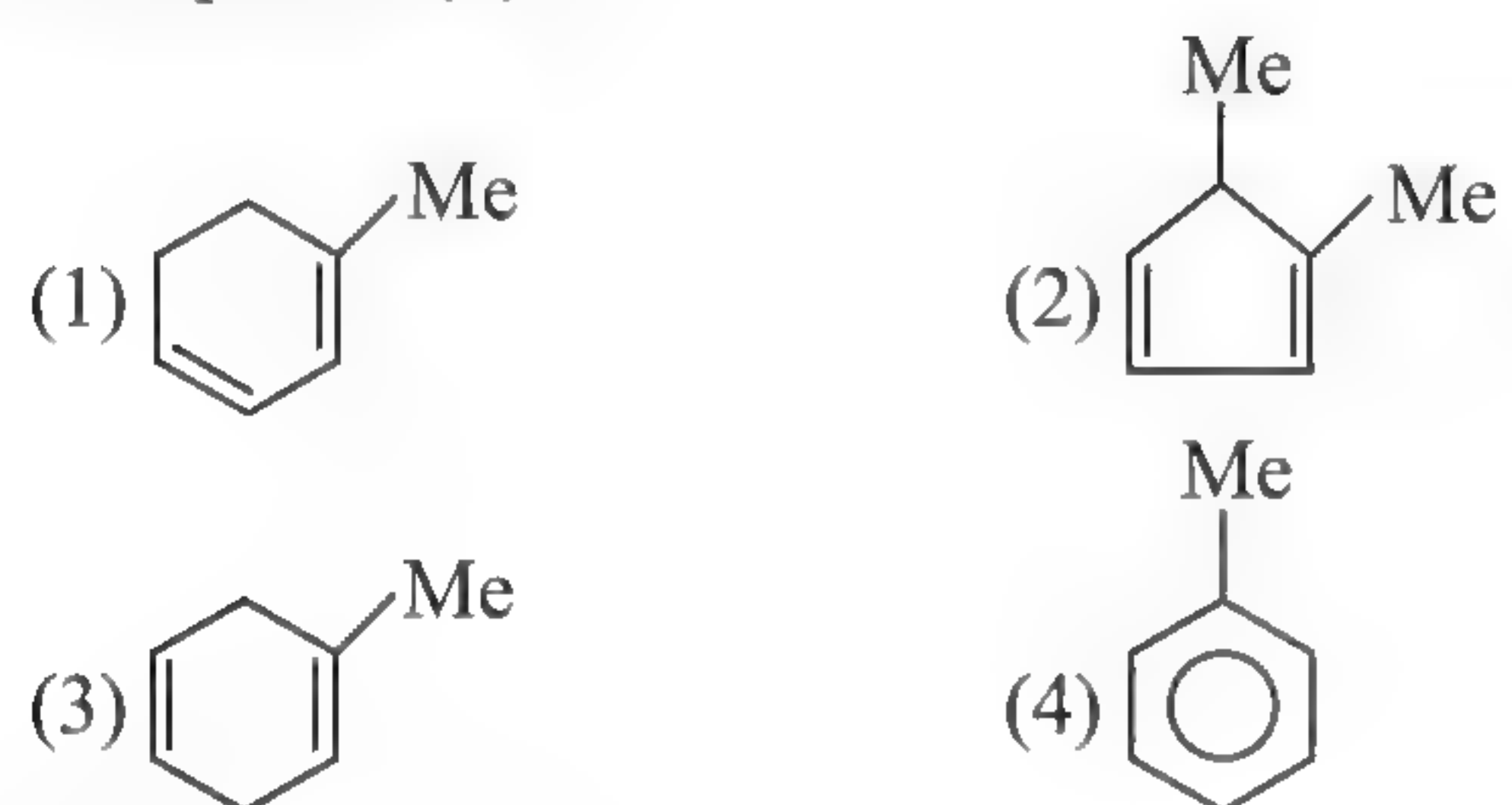
10. Compound (D) is:



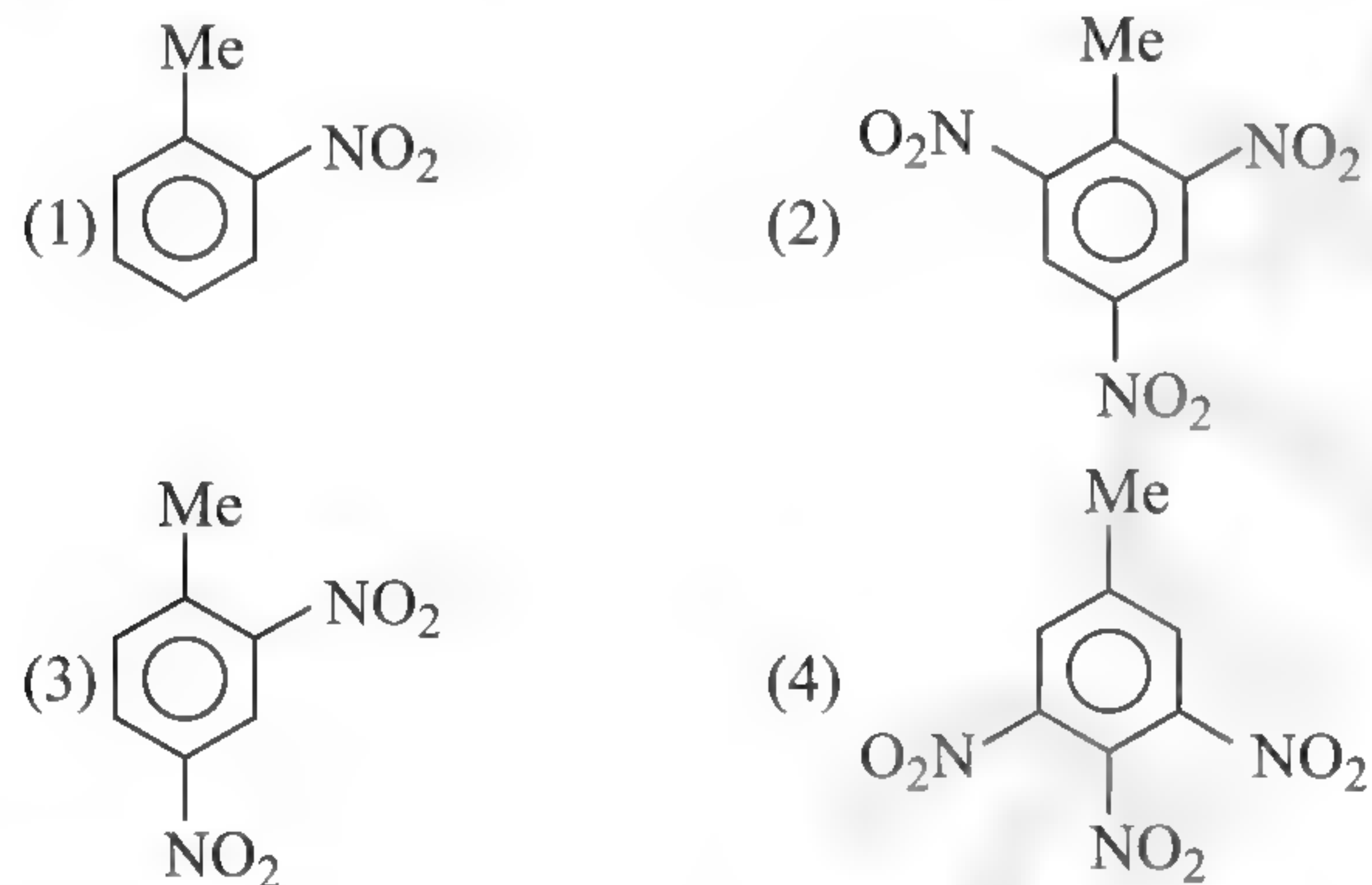
11. Compound (E) is:



12. Compound (F) is

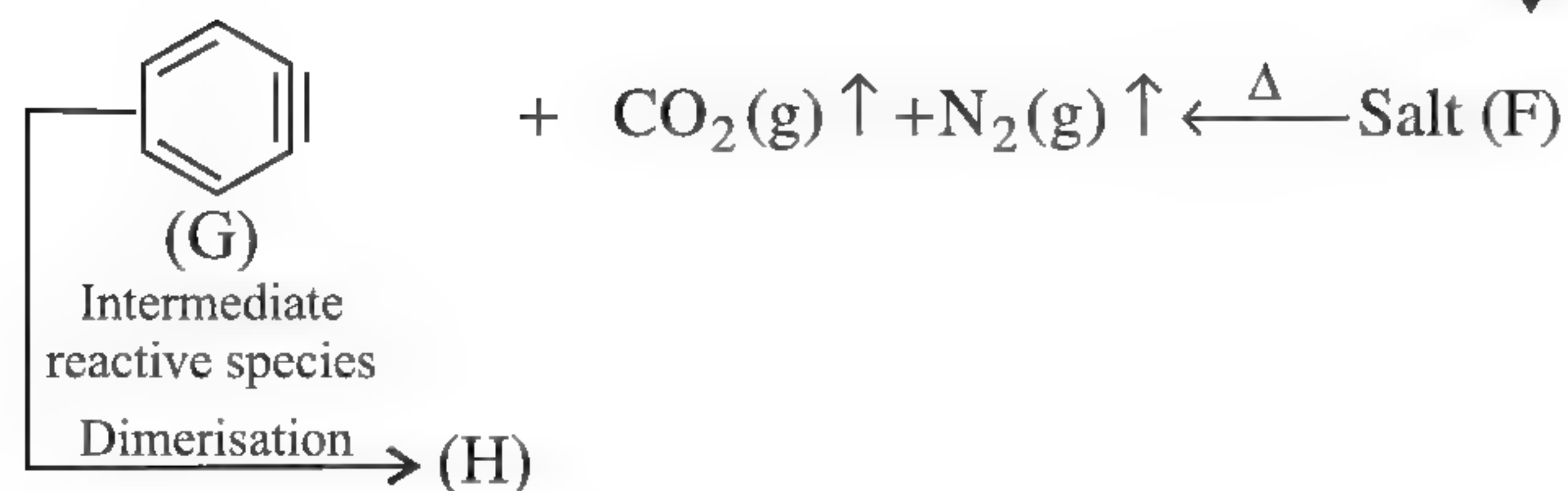
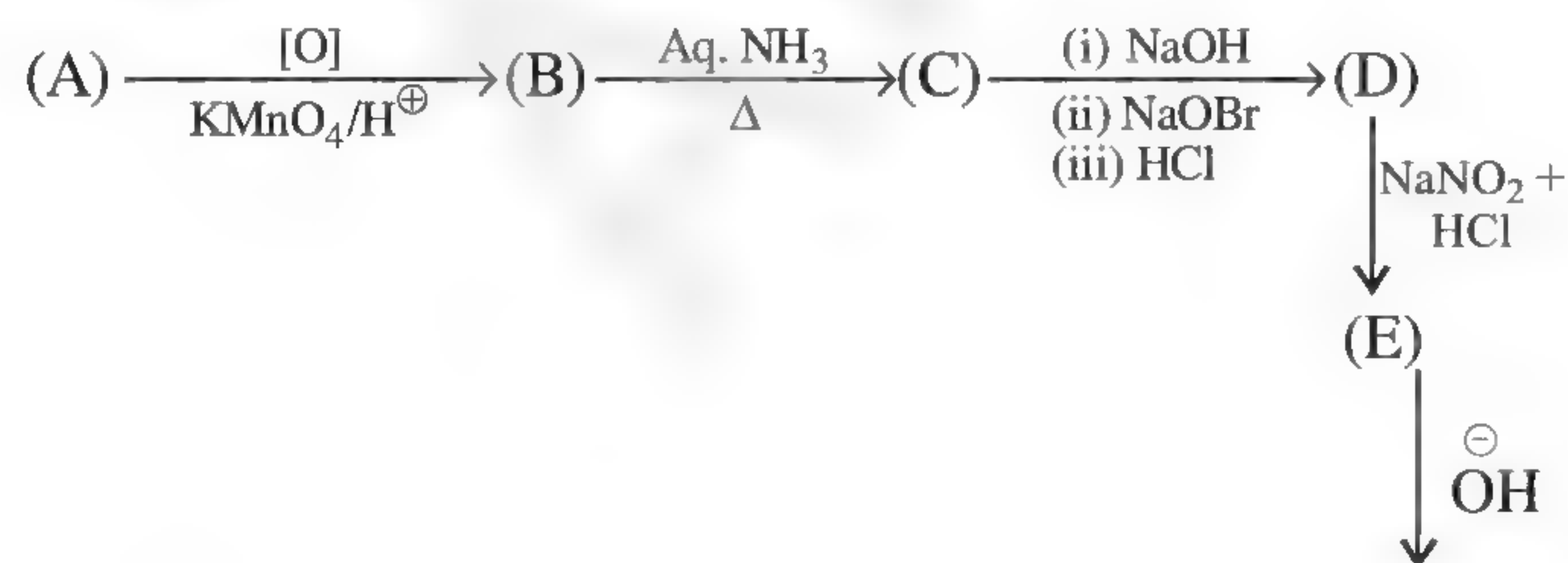


13. Compound (G) is:



Paragraph 3

A hydrocarbon (A) (C_8H_{10}) (E) is a steam volatile compound and on nitration gives two mononitro derivatives. (A) gives the following reactions.



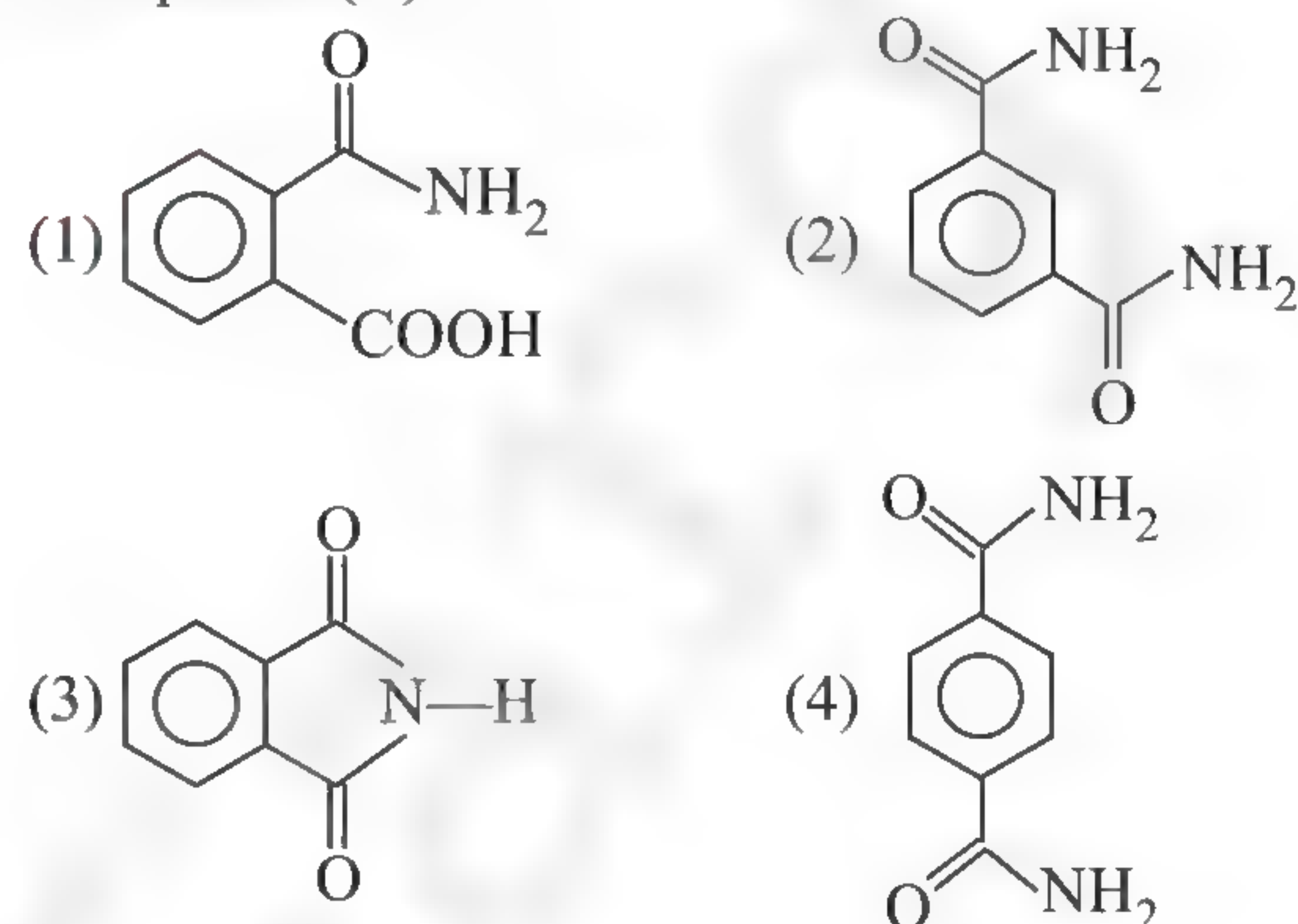
14. Compound (A) is:

- (1) Ethylbenzene (2) *p*-Xylene
 (3) *m*-Xylene (4) *o*-Xylene

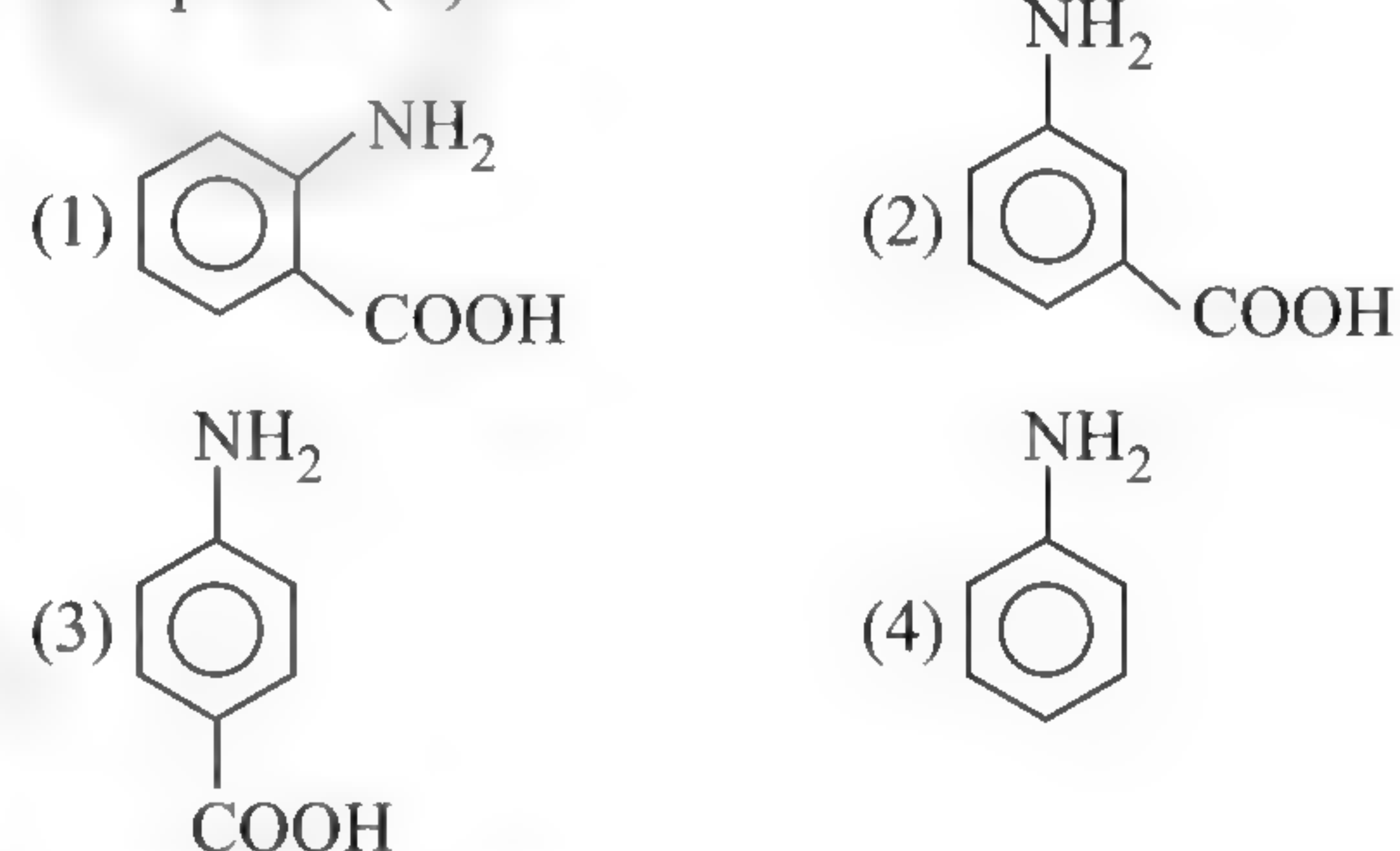
15. Compound (B) is:

- (1) Phthalic acid (2) Isophthalic acid
 (3) Terephthalic acid (4) Benzoic acid

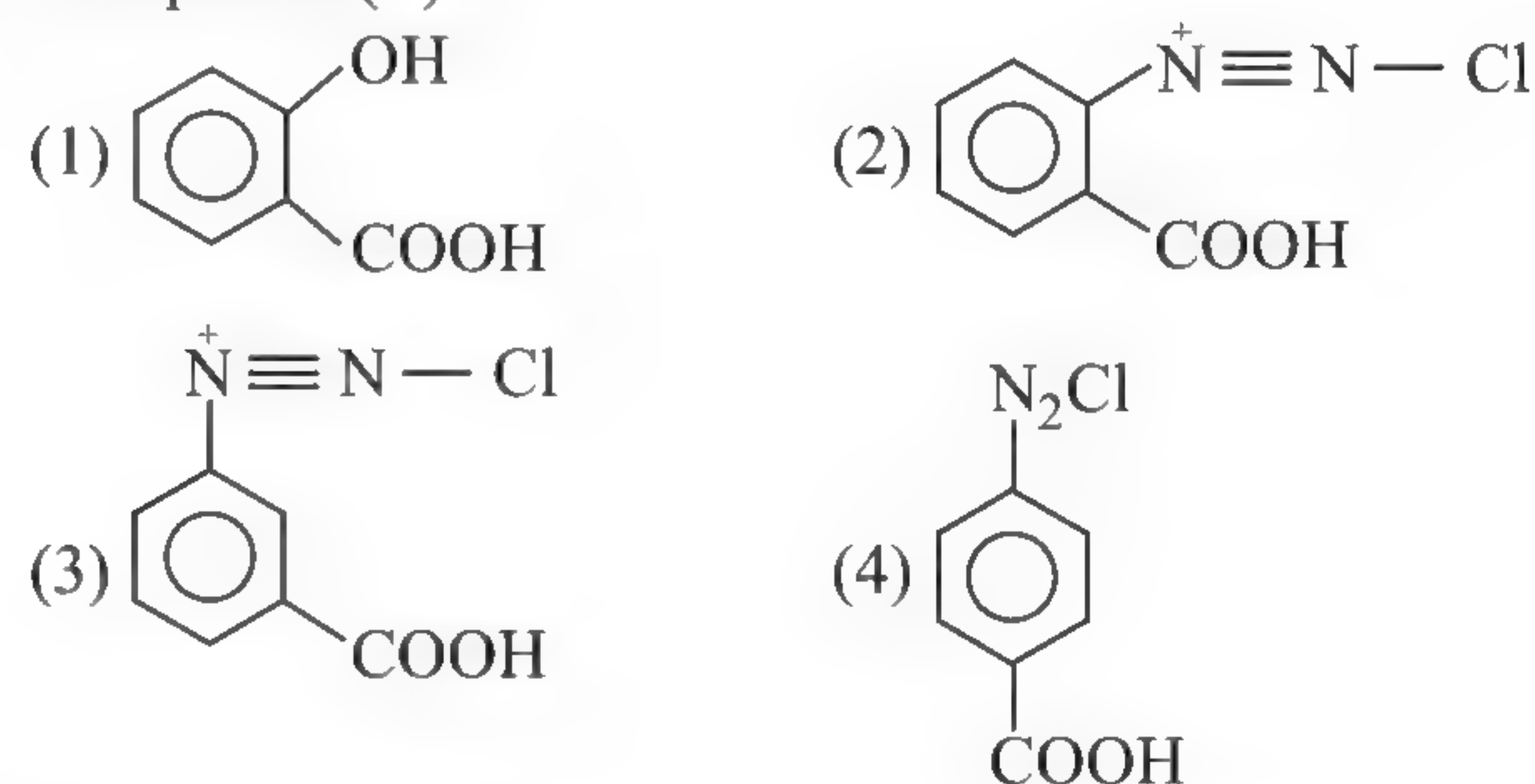
16. Compound (C) is:



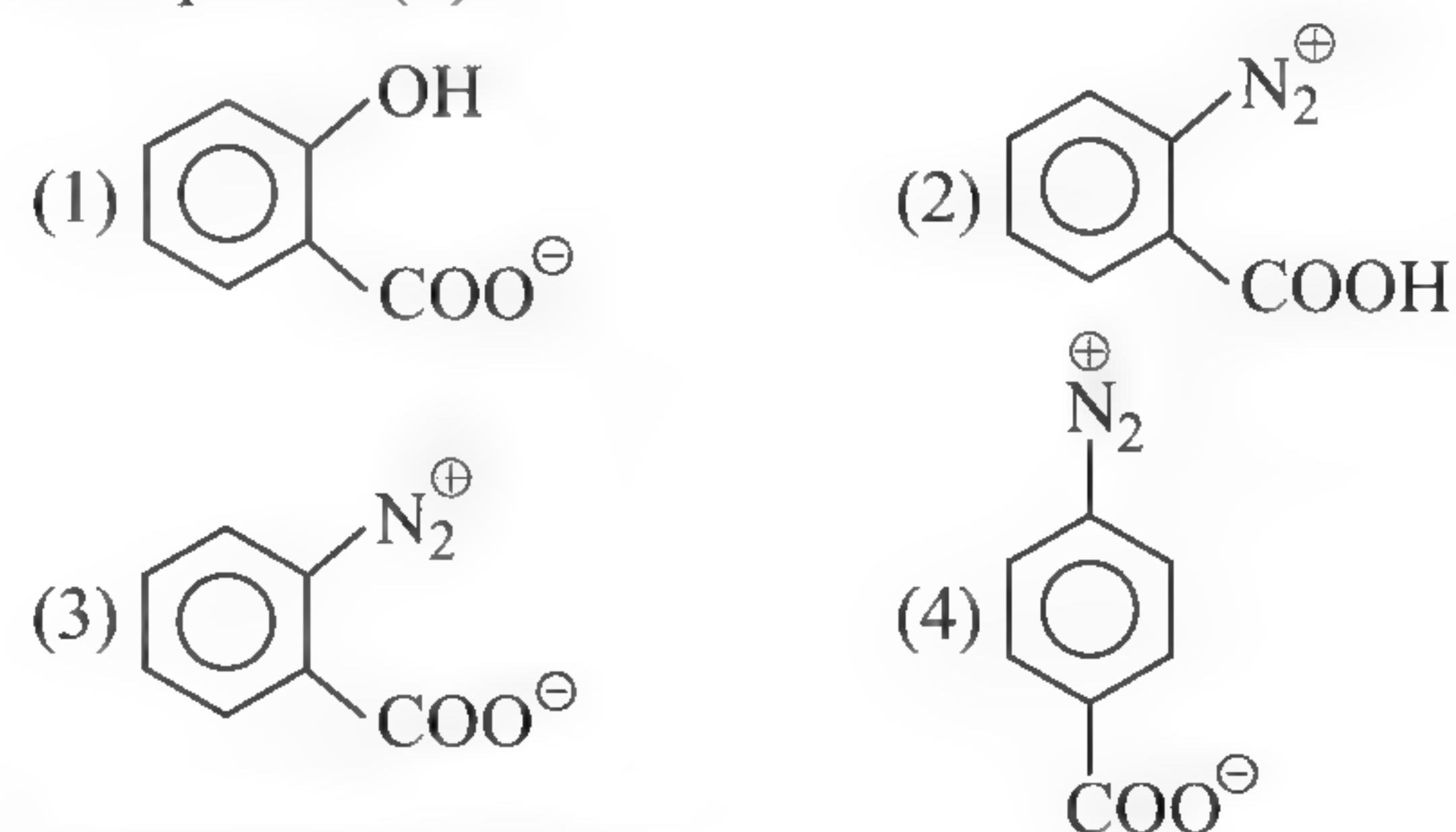
17. Compound (D) is:



18. Compound (E) is:



19. Compound (F) is:



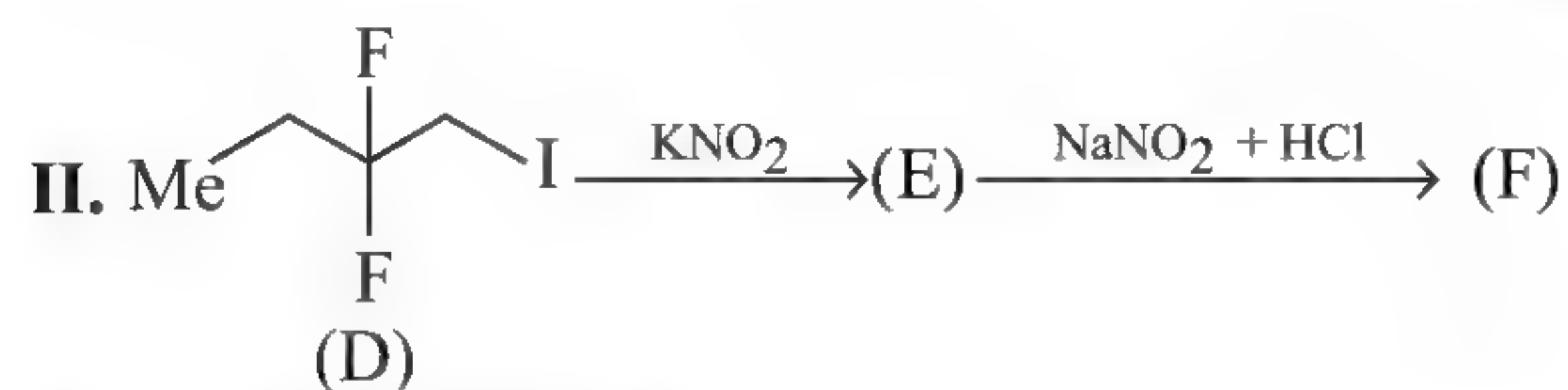
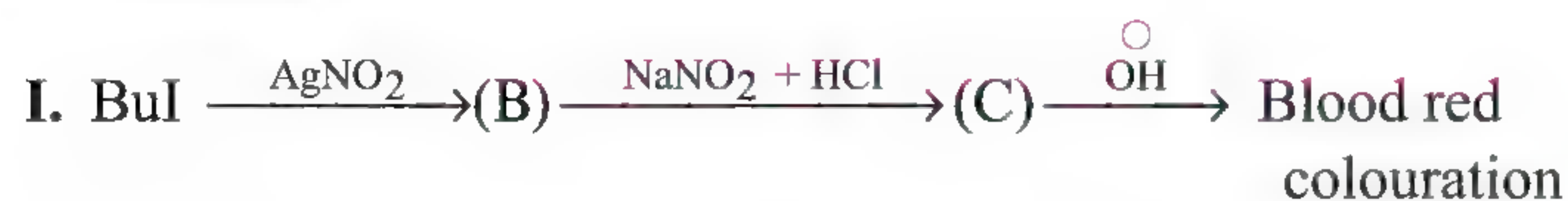
20. The name of (H) is:

- (1) Dibenzocyclobutane (2) Dibenzocyclobutadiene
 (3) Dibenzocyclobutene (4) Benzocyclobutane

21. Degree of unsaturation (DU) in (H) is:

- (1) 7 (2) 8
 (3) 9 (4) 10

Paragraph 4



22. Compound (B) is:

- (1) $\text{Bu}-\text{NO}_2$ (2) $\text{Bu}-\text{O}-\text{N}=\text{O}$
 (3) Both (4) None

23. Compound (C) is:

- (1) $\text{C}_3\text{H}_7-\text{C}(\text{NO}_2)=\text{N.OH}$ (2) $\text{C}_3\text{H}_7-\text{C}(\text{ONO})=\text{N.OH}$
 (3) $\text{C}_3\text{H}_7-\text{CH}(\text{NO}_2)-\text{N}=\text{O}$ (4) $\text{C}_3\text{H}_7-\text{CH}(\text{ONO})-\text{N}=\text{O}$

24. Compound (E) is:

- (1) $\text{Me} \xrightarrow{\text{F}} \text{Me}-\text{C}(\text{F})_2-\text{NO}_2$ (2) $\text{Me} \xrightarrow{\text{F}} \text{Me}-\text{C}(\text{F})_2-\text{ONO}$
 (3) Both (4) None

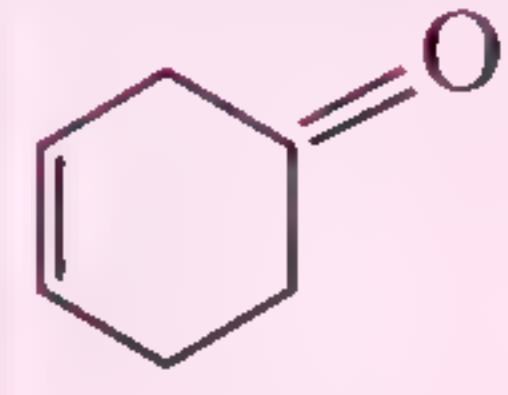
25. Compound (F) is:

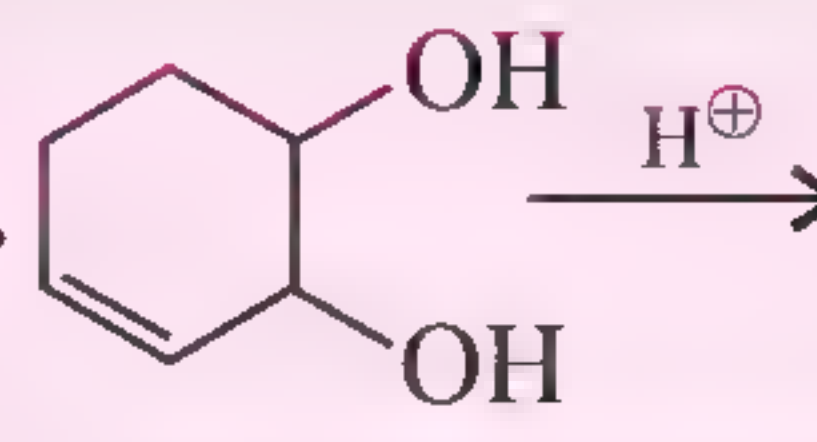
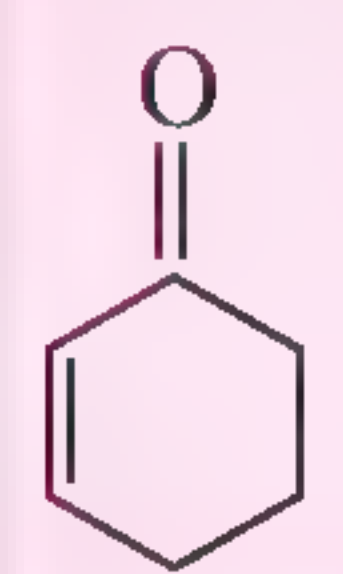
- (1) $\text{Me} \xrightarrow{\text{F}} \text{Me}-\text{C}(\text{F})_2-\text{NO}_2$ (2) $\text{Me} \xrightarrow{\text{F}} \text{Me}-\text{C}(\text{F})_2-\text{ONO}$
 (3) No reaction (4) Both (1) and (2)

Matrix Match Type

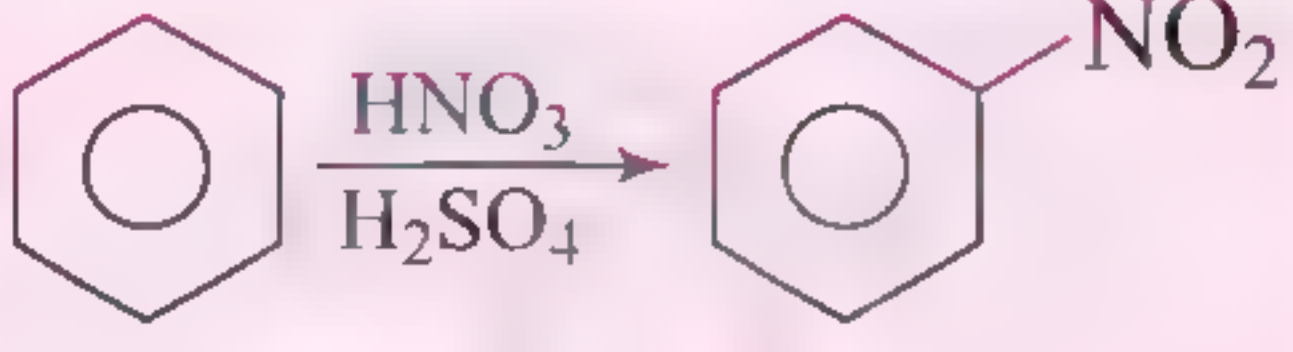
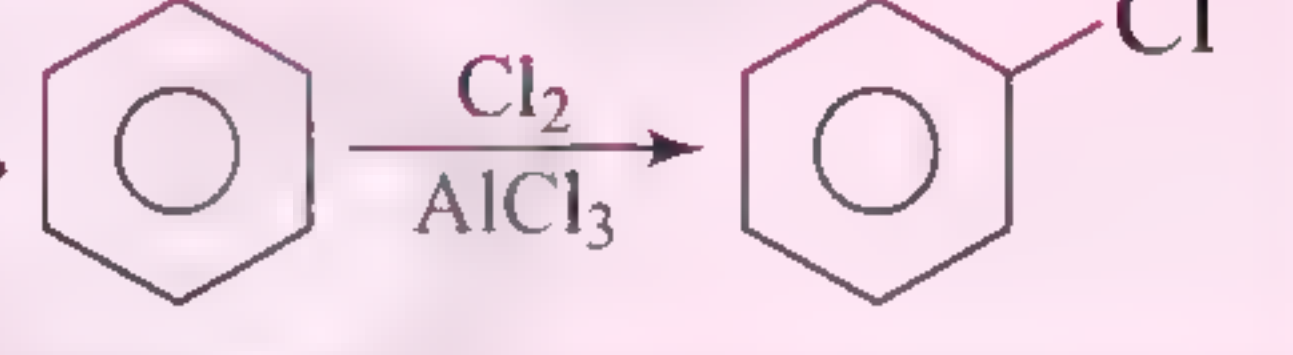
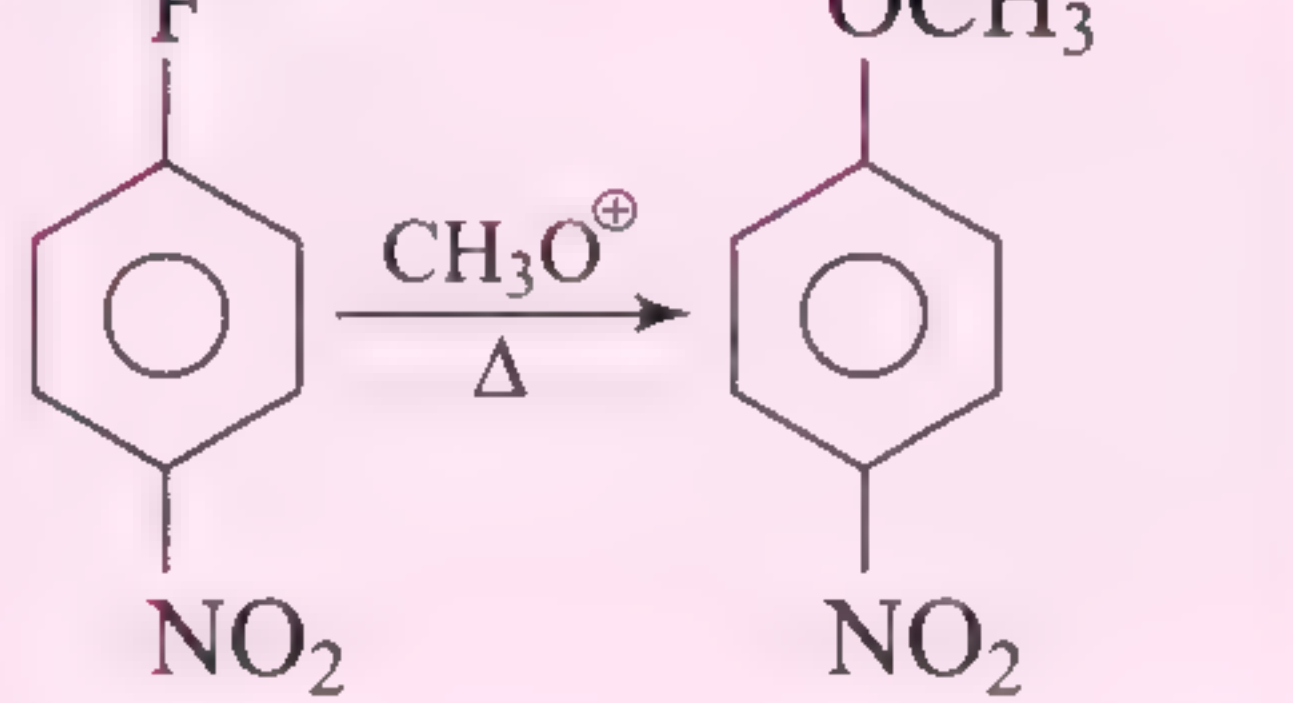

Match the compounds/reactions in column I with their characteristic(s)/reaction(s)/mechanisms/stereochemistry/isomer(s) given in column II. Matching can be one or more than one.

1. Match the Column.

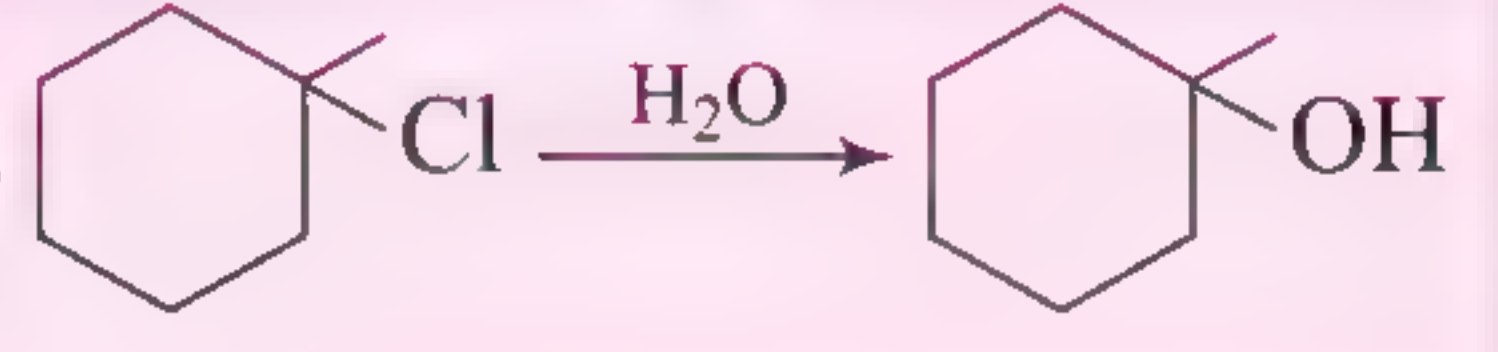
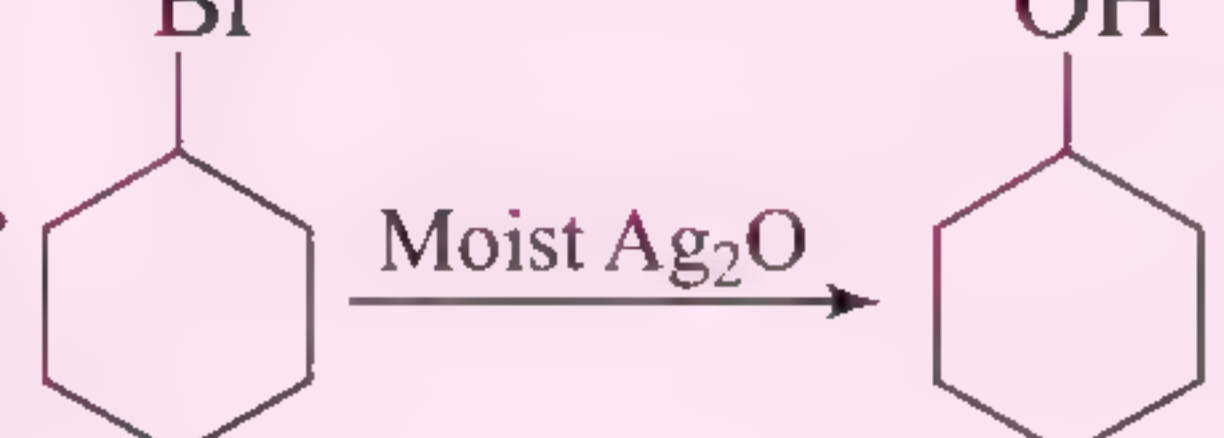
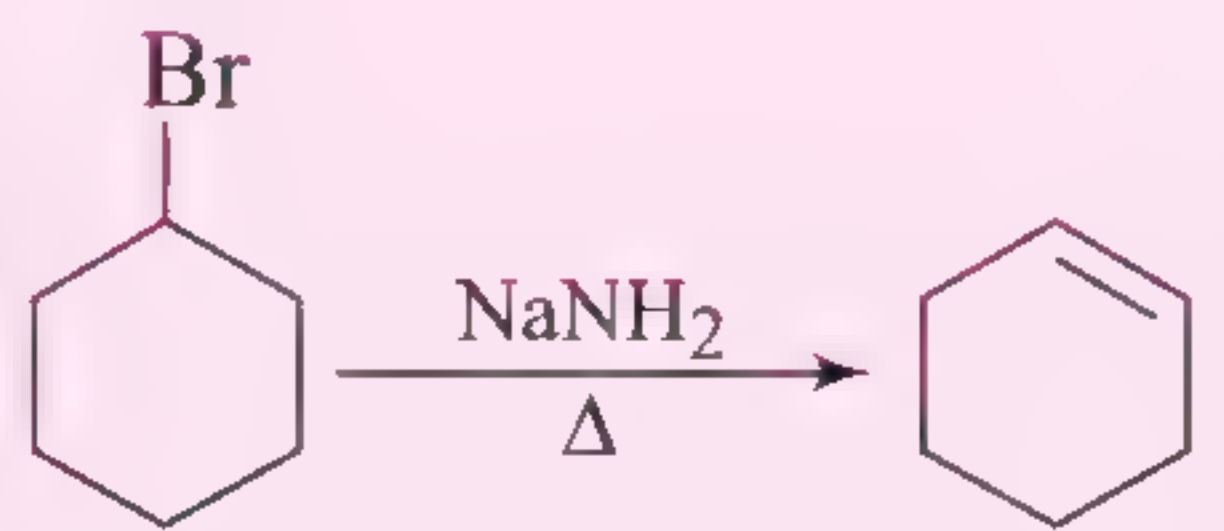
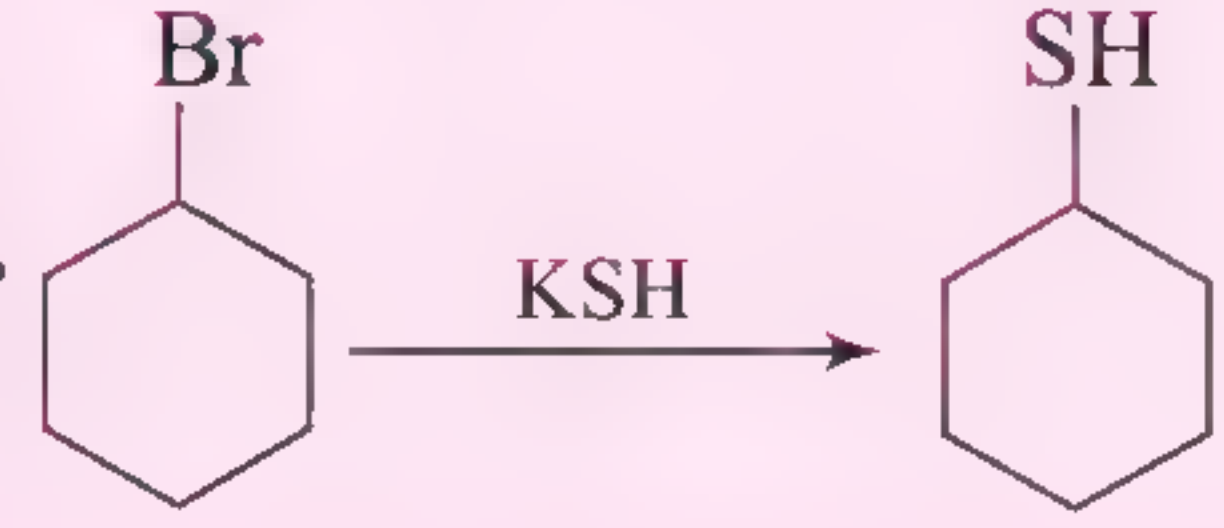
Column-I Reaction	Column-II Characteristics
a. $\text{CH}_3\text{CH}=\text{CHCH}_3 \xrightarrow[\text{(ii) Aq. NaOH}]{\text{(i) H}_2\text{C}=\text{CBr}_2/\Delta}$	p. Birch reduction
b. $\text{Cyclohexyl-Br} \xrightarrow[\text{(ii) PCC}]{\text{(i) Aq. NaOH}}$	q. 
c. $\text{Cyclohexyl-OMe} \xrightarrow[\text{(ii) H}_3\text{O}^+/\text{H}_2\text{O}]{\text{(i) Li/Liq. NH}_3}$	r. (4 + 2) Addition reaction

d. 	s. MeOH
	t. 


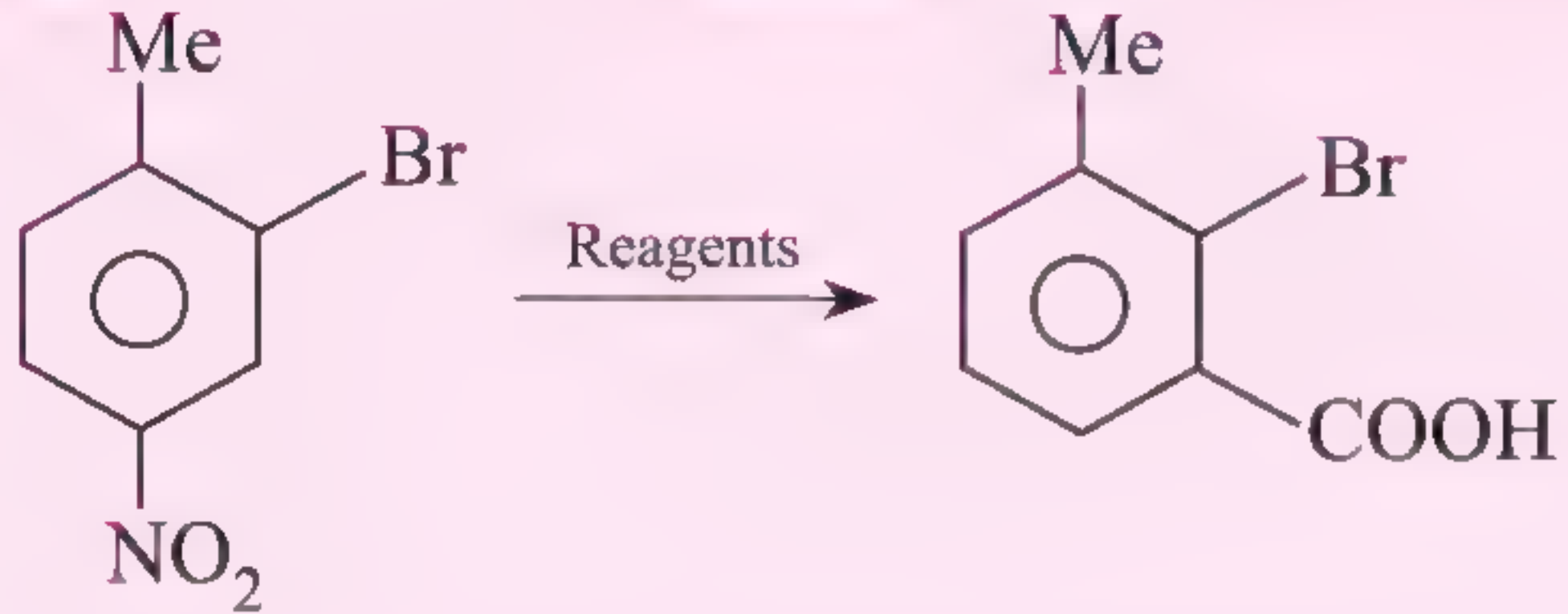
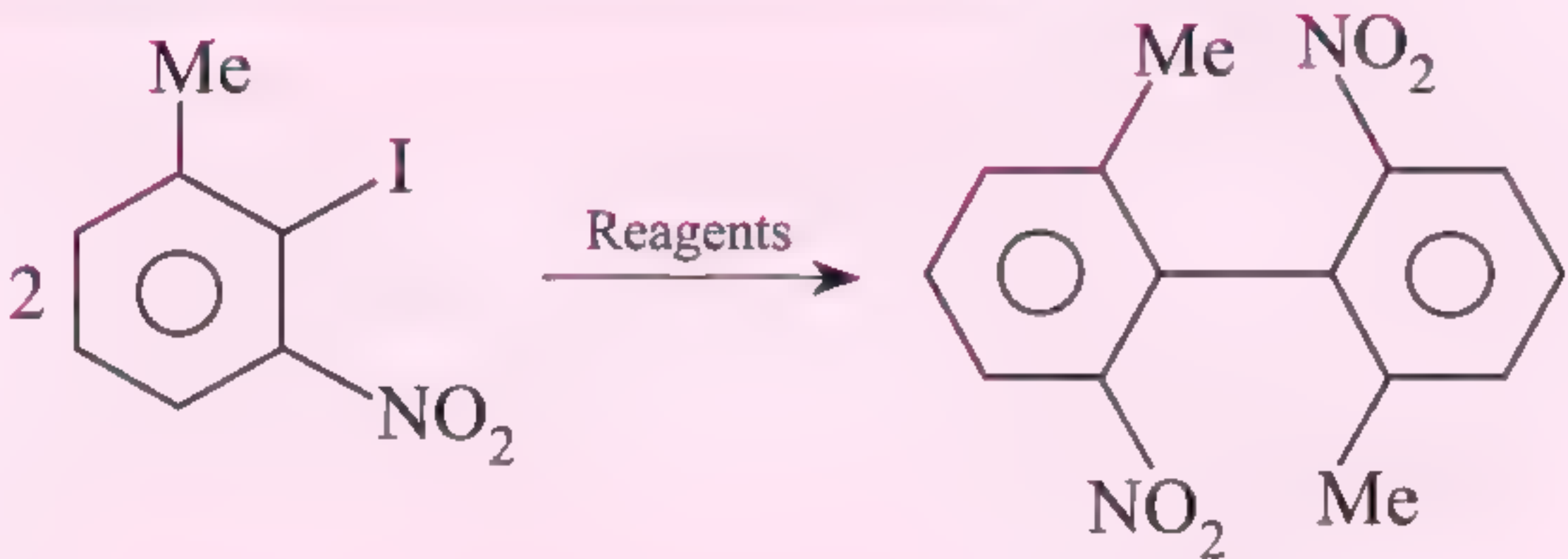
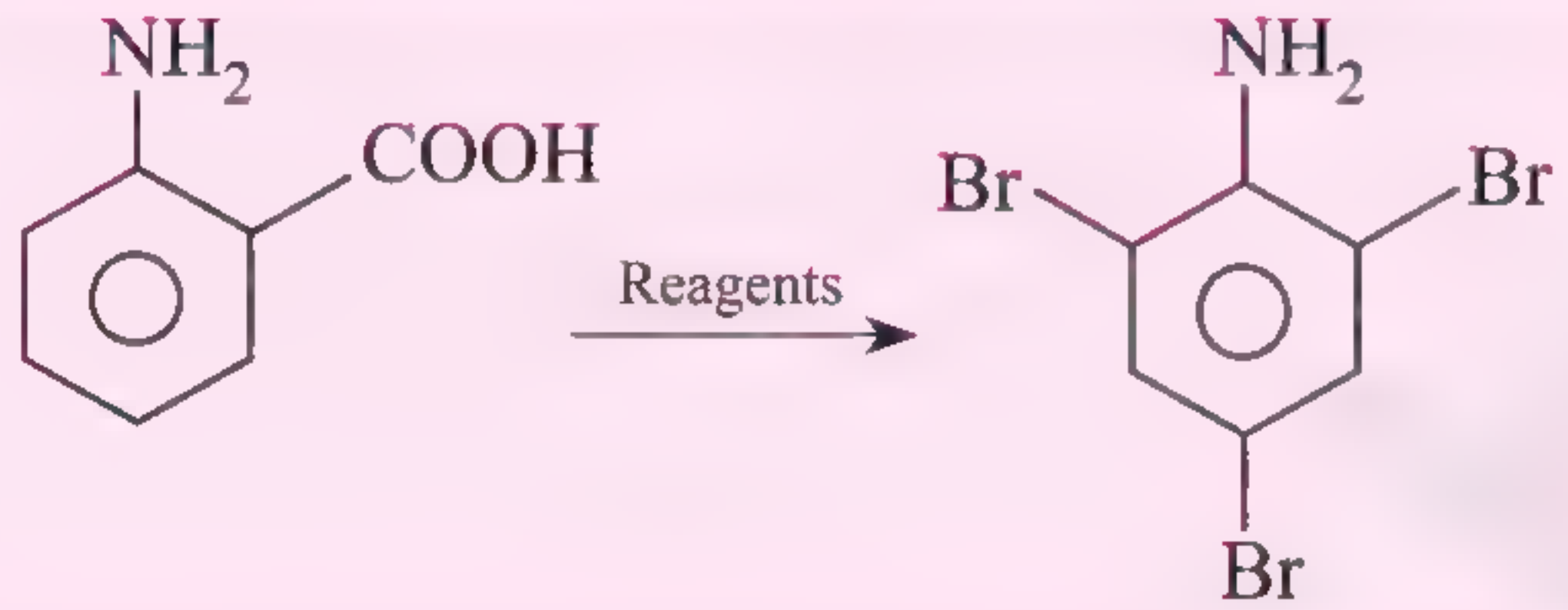
2. Match the Column.

Column-I	Column-II
a. 	p. Substitution reaction
b. 	q. Addition reaction
c. 	r. Carbocation is intermediate
d. 	s. Carbanion is intermediate

3. Match the Column.

Column-I	Column-II
a. 	p. Substitution reaction
b. 	q. Elimination reaction
c. 	r. Carbocation is intermediate
d. 	s. Carbanion is intermediate

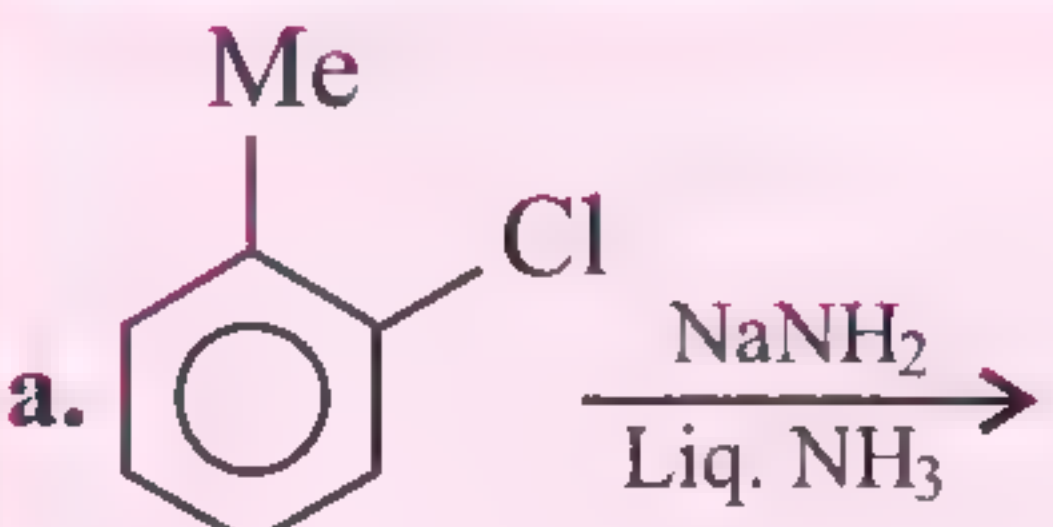
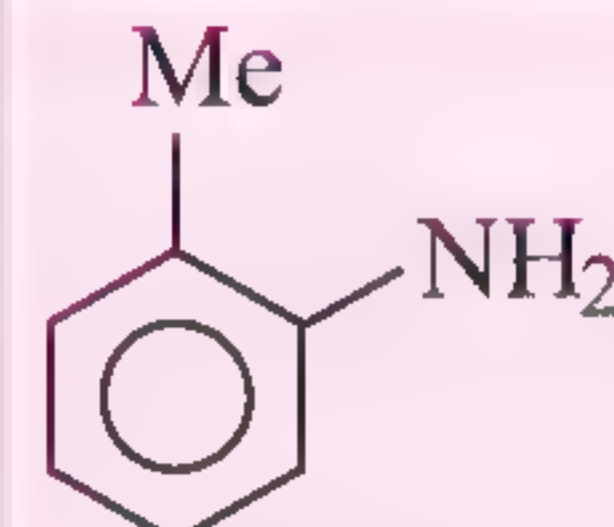
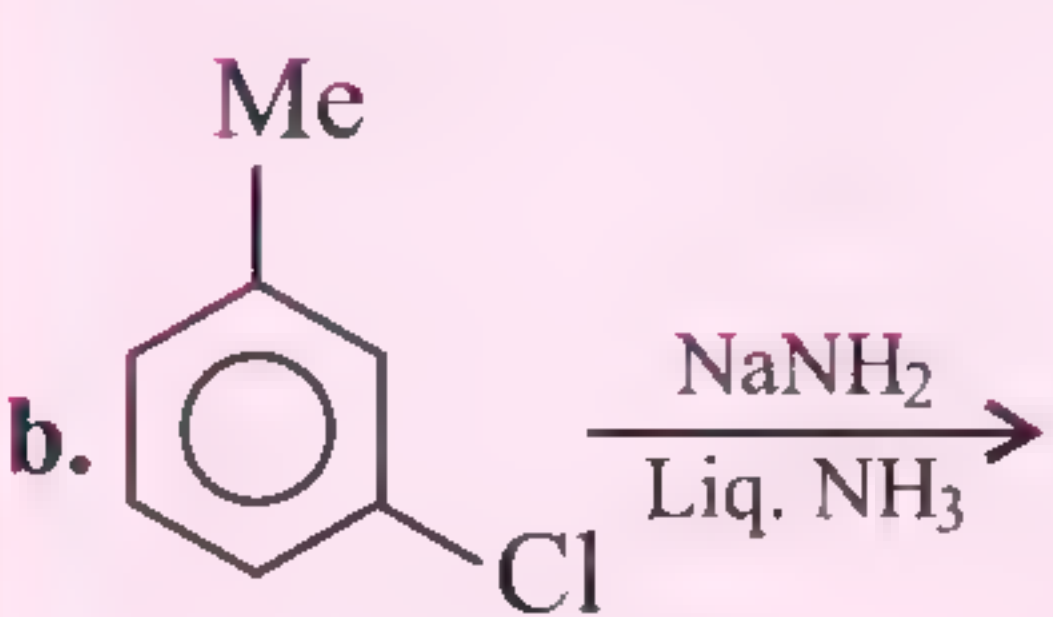
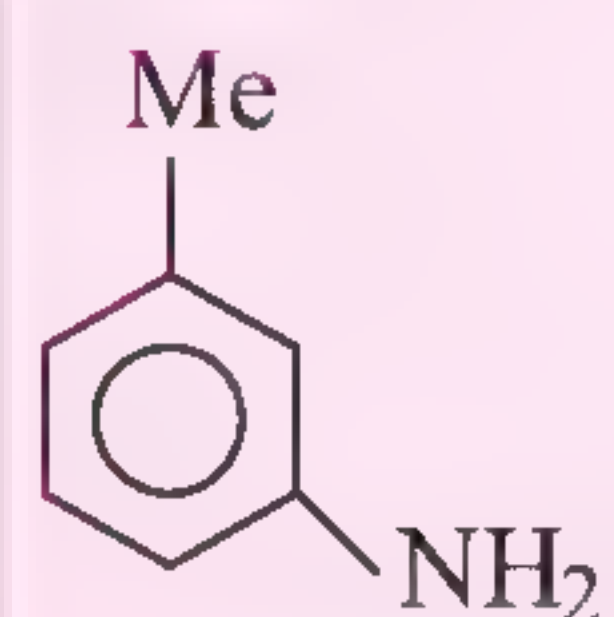
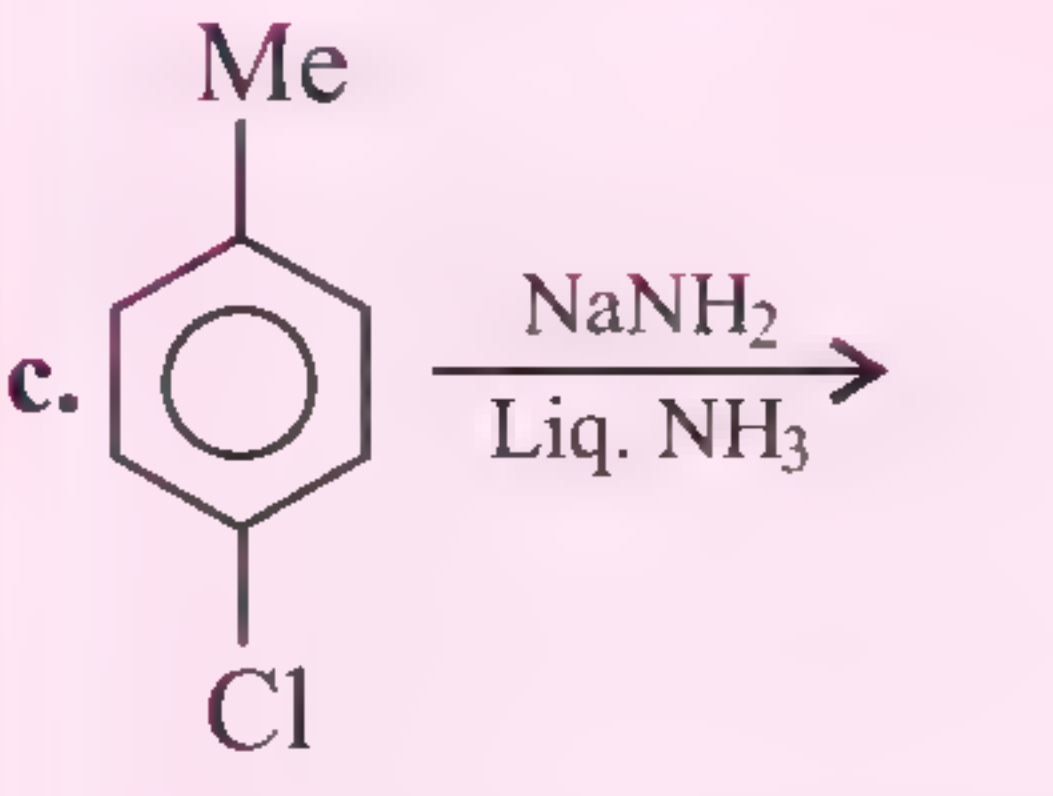
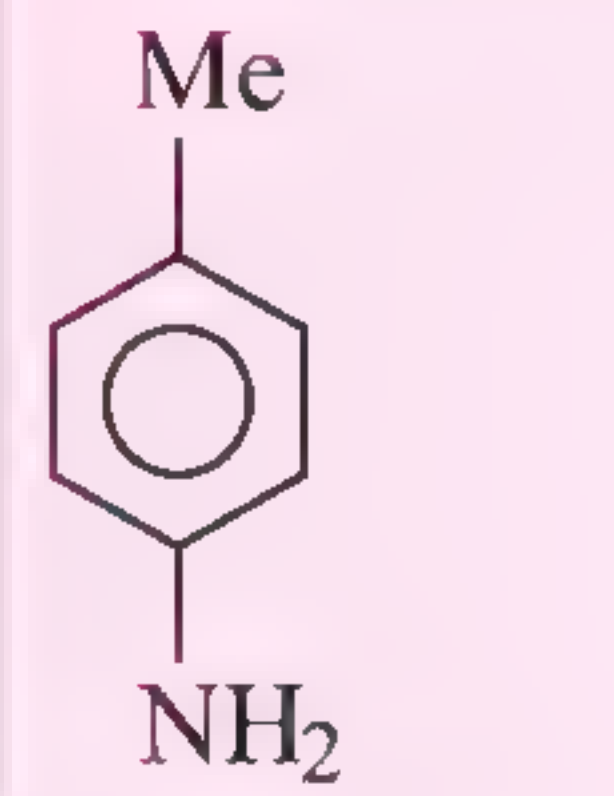
4. Match the items given in column I with those in column II and III.

Column I		Column II		Column III	
Reactions		Reagents		Characteristics	
a		i	Cu/ Δ	p	Borodine Hunsdiecker reaction
b		ii	$\text{BrO}_3^- + \text{Br}^- + \text{H}^+$	q	Atrop-isomerism
c		iii	(i) PbO (ii) Br_2/CCl_4	r	Ipsso-substitution
d		iv	(i) KCN (ii) Aq. $\text{C}_2\text{H}_5\text{OH}$	s	Von-richter reaction
				t	Ullmann reaction

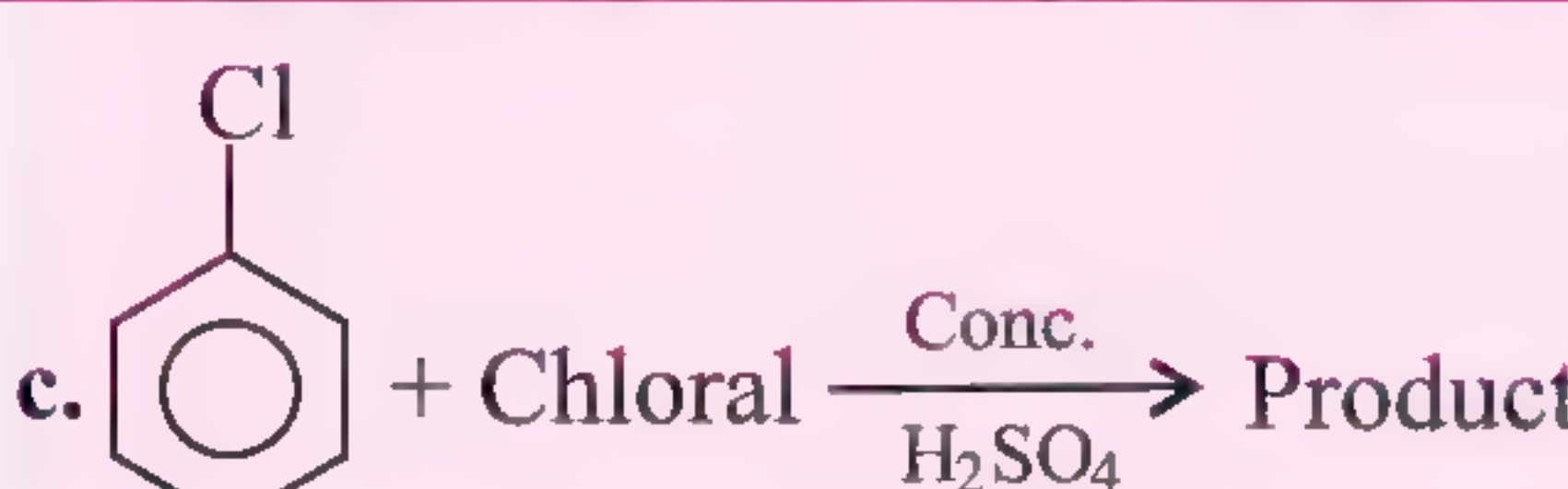
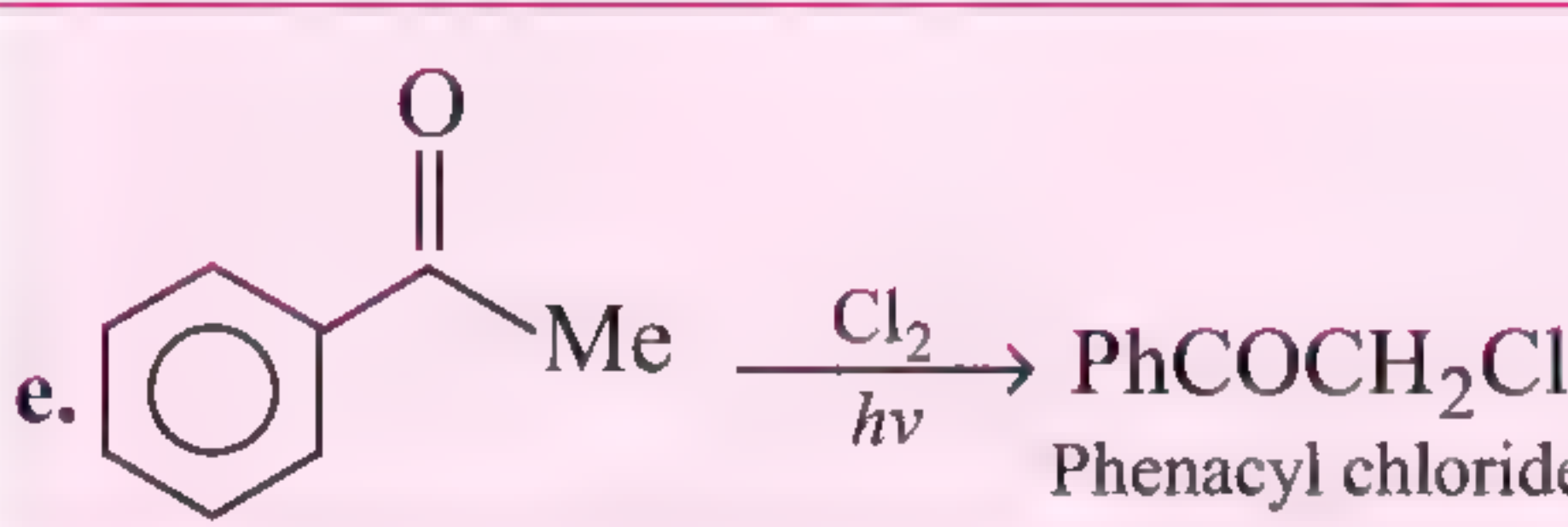
5. Match the Column.

Column-I Compound	Column-II Formula	
a. Freon-12	p.	$\text{C}_2\text{F}_3\text{CHClBr}$
b. Freon-13	q.	CCl_4
c. Freon-22 or R-22	r.	CF_2Cl_2
d. Compound 66	s.	CF_3Cl
e. Compound 666	t.	$\text{C}_2\text{F}_2\text{Cl}_4$
f. Halothane	u.	Perchlorobenzene
g. Pyrene	v.	B.H.C.

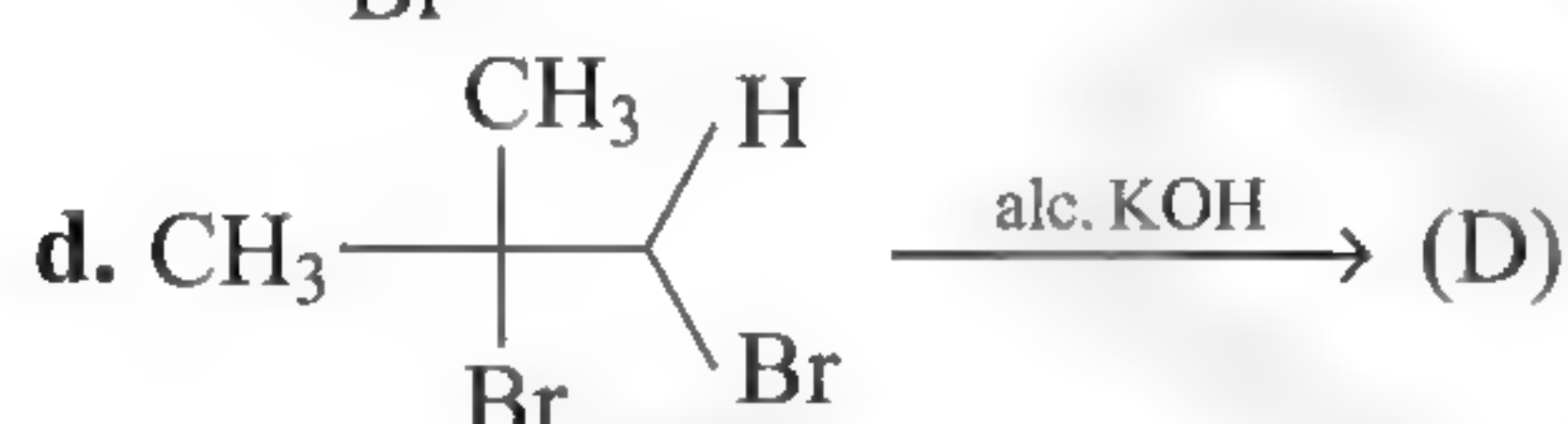
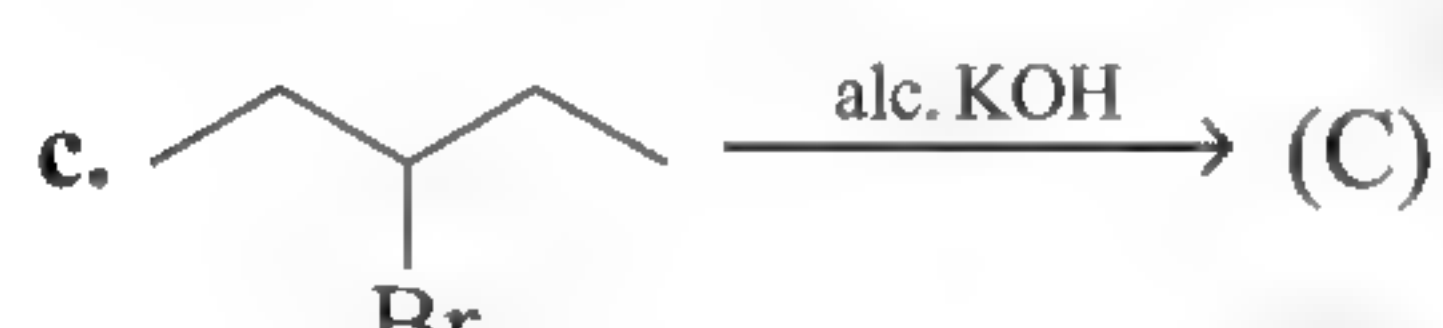
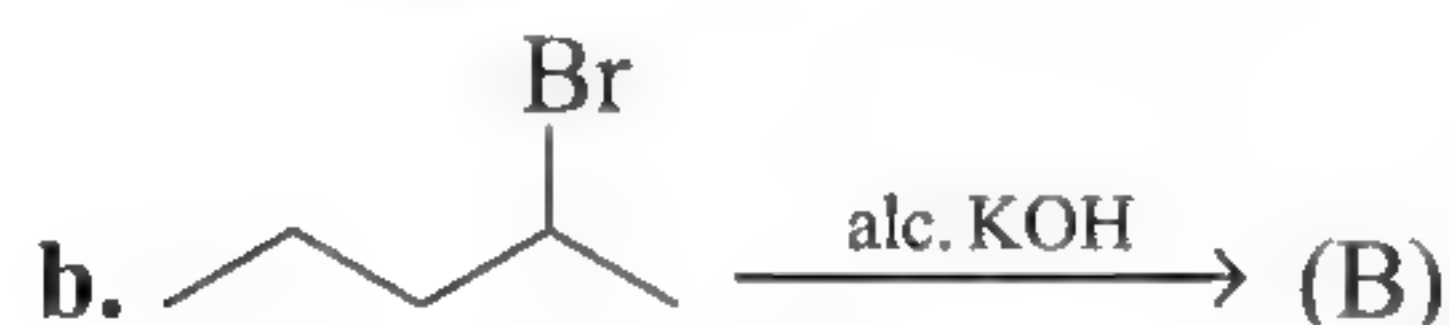
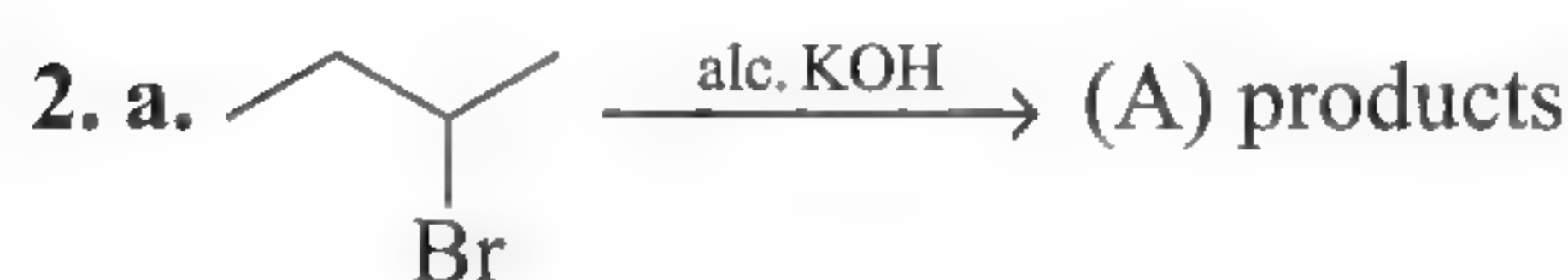
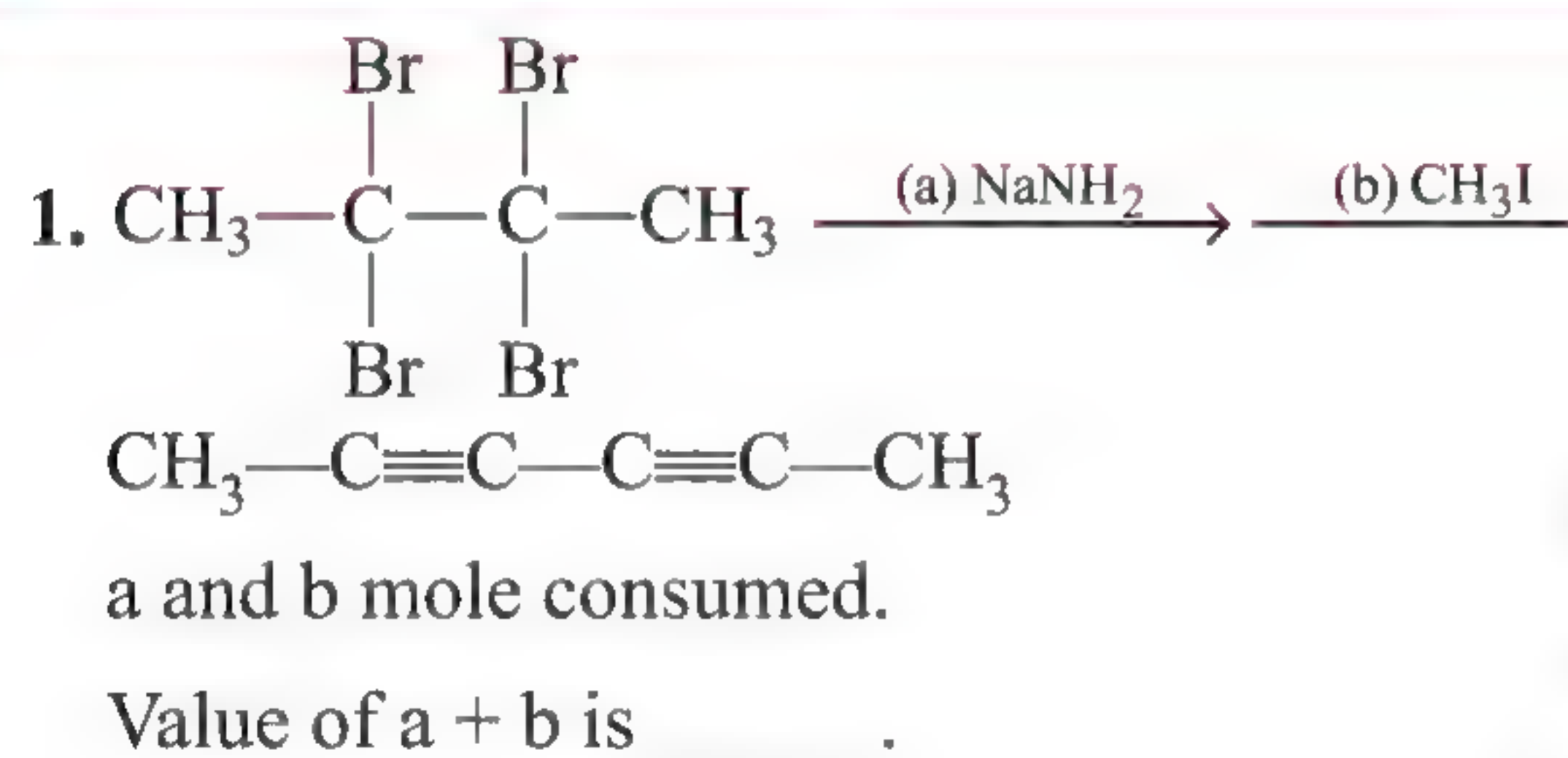
6. Match the Column.

Column-I Reaction	Column-II Products/mechanism	
a. 	p.	
b. 	q.	
c. 	r.	
	s.	ArSN (elimination addition) reaction

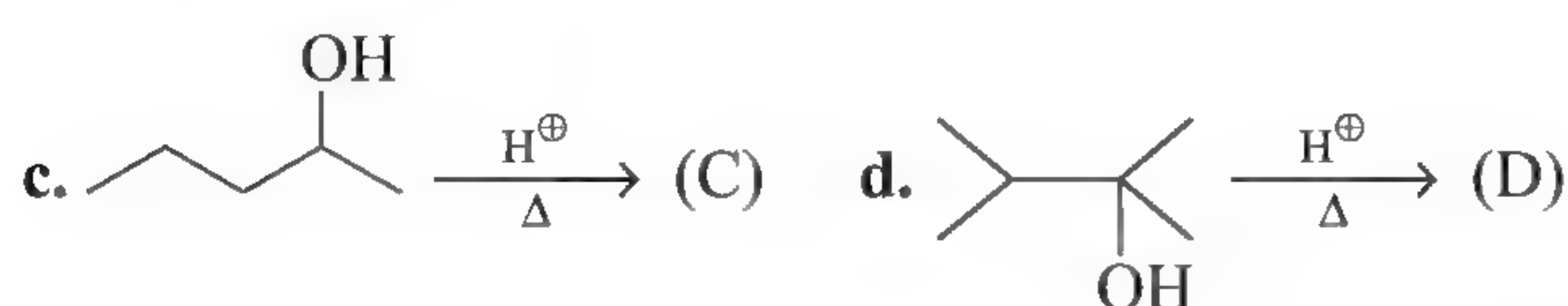
7. Match the Column.

Column-I Reaction	Column-II Characteristics
a. $\text{CHCl}_3 + \text{HNO}_3 \rightarrow$ An insecticide and tear gas	p. Gammaxene
b. Benzene + $\text{Cl}_2 \xrightarrow{h\nu}$ Product	q. Borodine–Hunsdiecker reaction
c.  + Chloral $\xrightarrow[\text{H}_2\text{SO}_4]{\text{Conc.}}$ Product	r. Chloropicrin
d. Silver acetate $\xrightarrow[\text{CCl}_4]{\text{Br}_2}$ CH_3Br	s. Compounds containing oxygen
e.  $\xrightarrow[h\nu]{\text{Cl}_2}$ PhCOCH ₂ Cl Phenacyl chloride	t. Dichlorodiphenyl trichloroethane
	u. Used as a lachrymator (weeping gas). Used to disperse the mob by police.

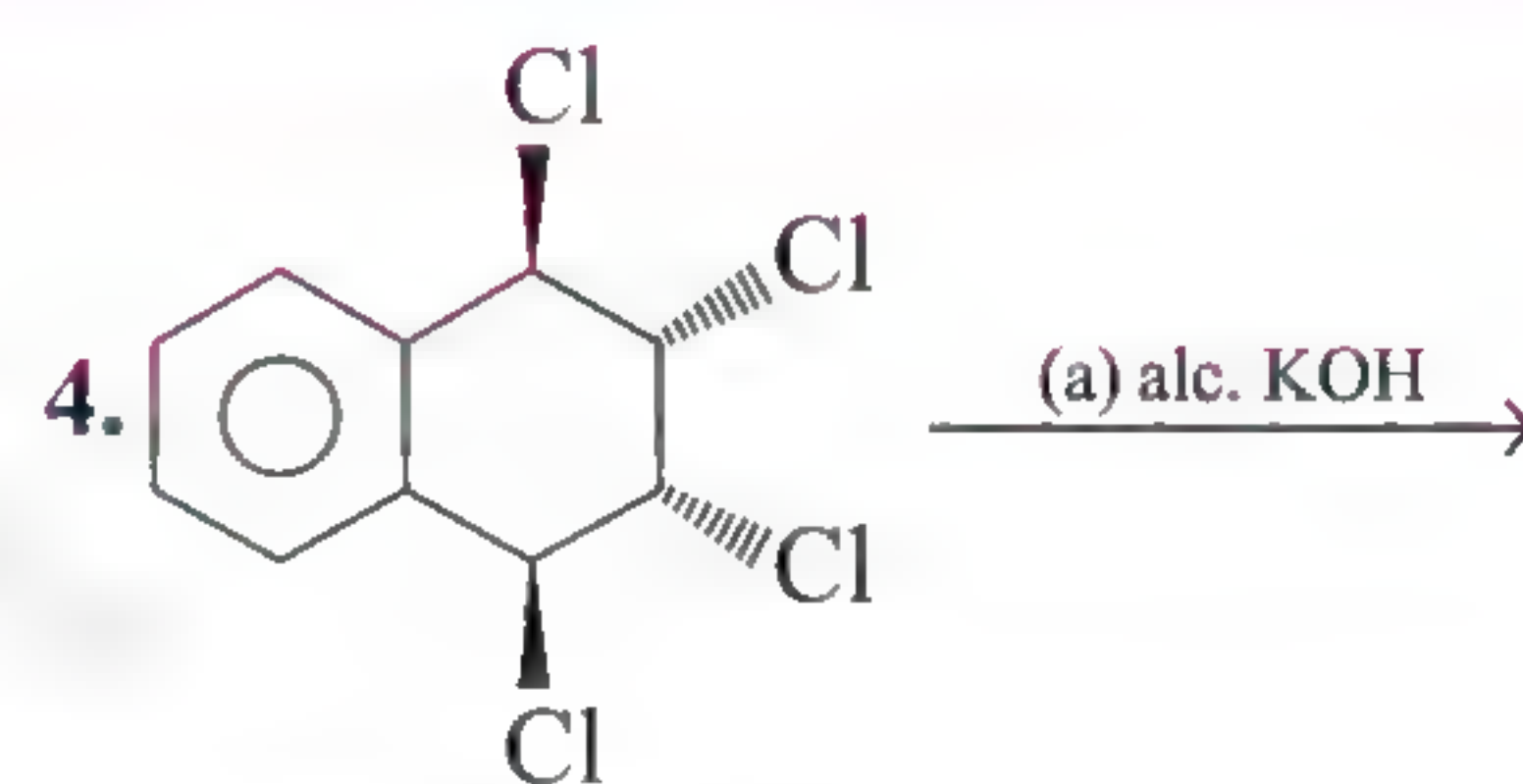
Numerical Value Type



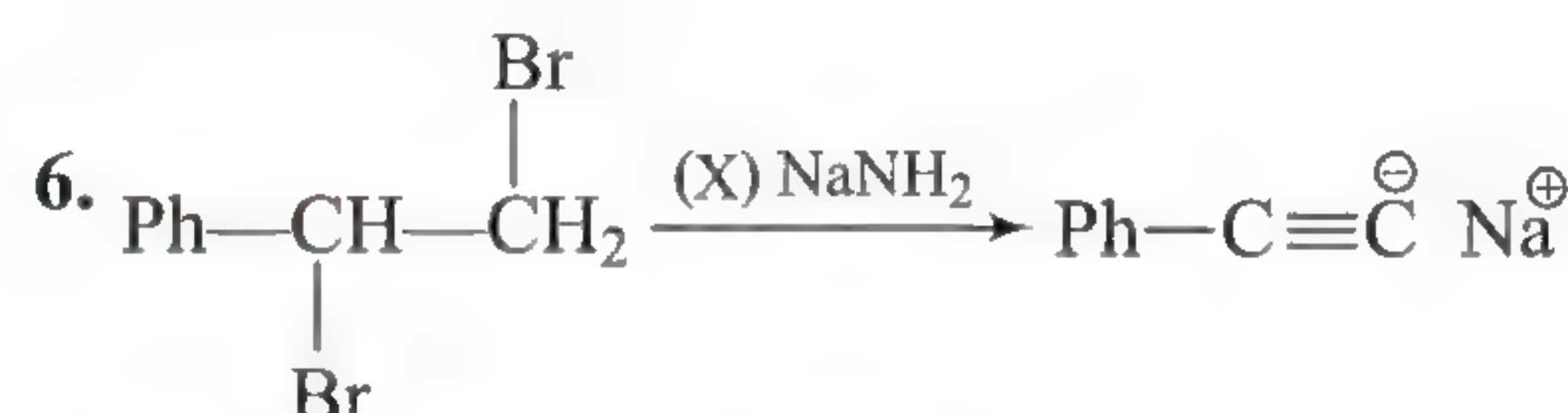
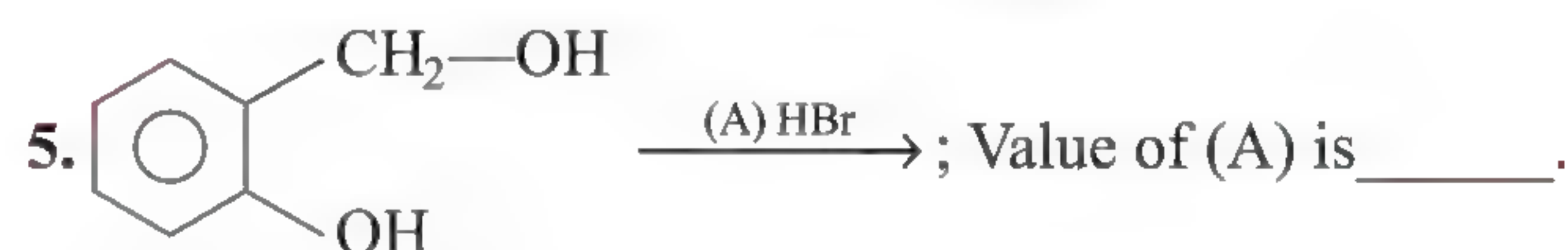
Sum of A + B + C + D is _____.



Total number of product obtained in above reactions including minor product is (including stereoisomer) _____.

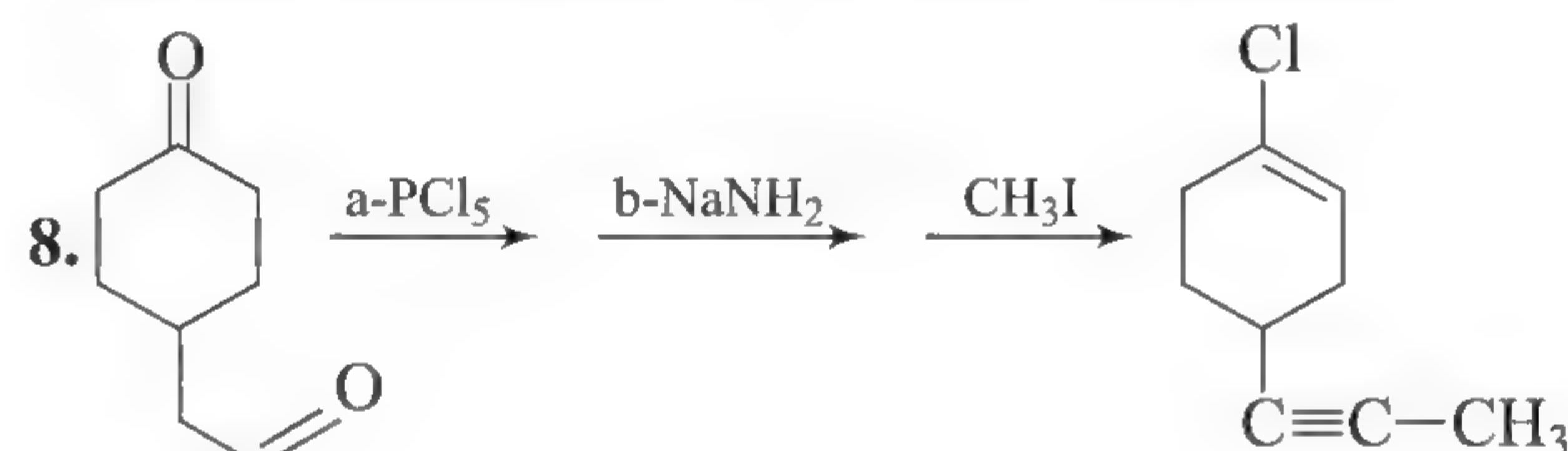


Moles of alc. KOH consumed are _____.

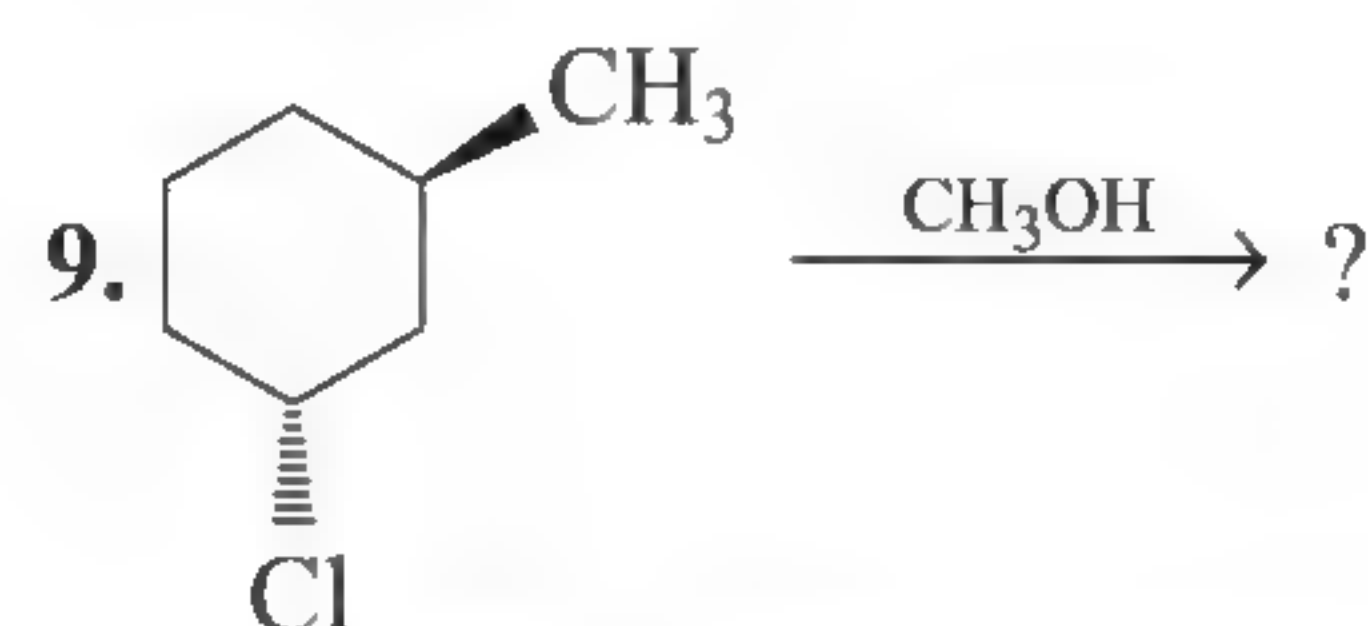


Find out the value of (X).

7. How many isomer of $\text{C}_4\text{H}_9\text{Br}$ when reacts with NaNH_2 diastereomers will form? (excluding stereoisomer)



Sum of a + b _____.



X = Total number of substitution and elimination product(s). Find the value of X.

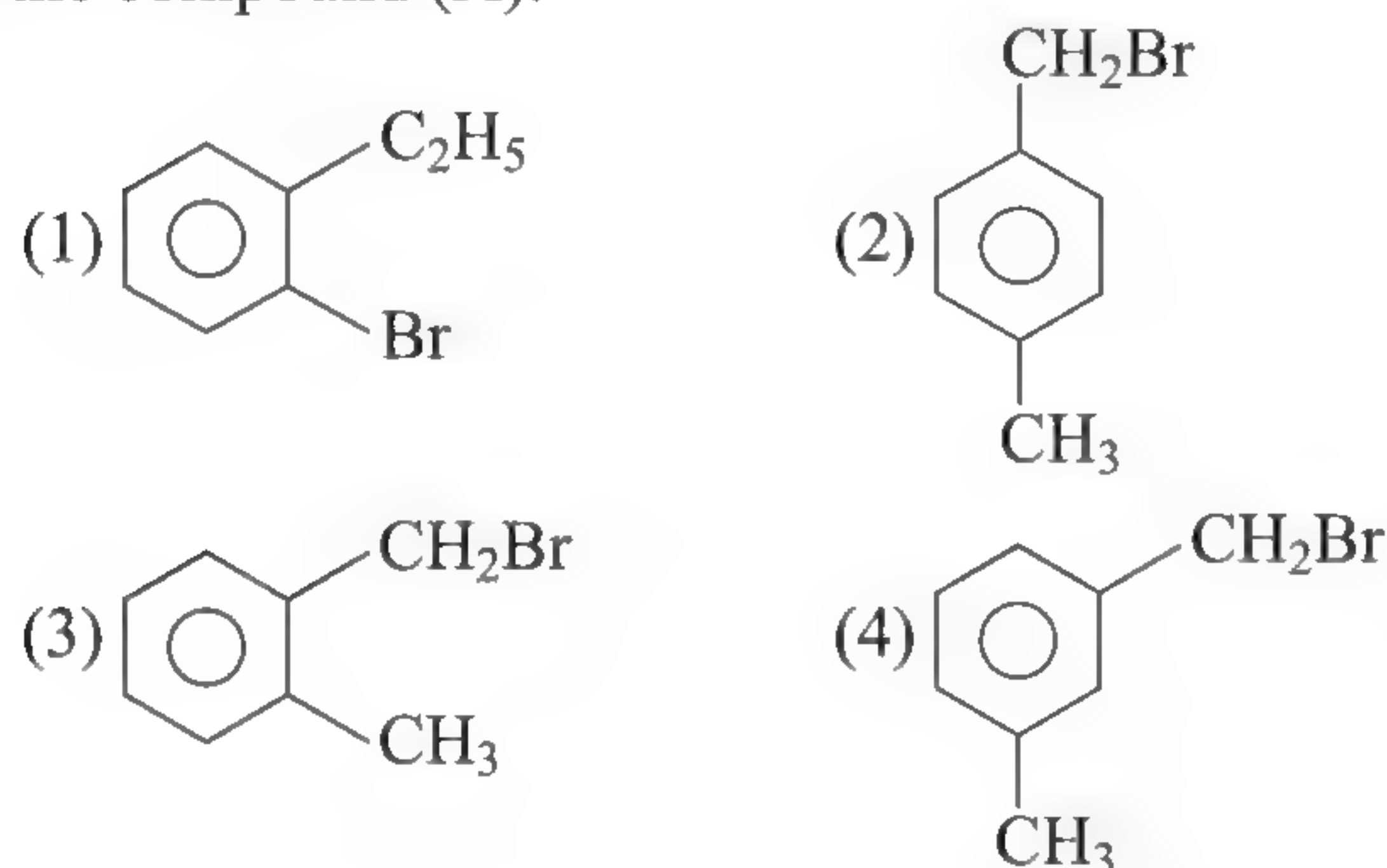
10. 1,2-Dibromopropane on treatment with X moles of NaNH_2 followed by treatment with $\text{C}_2\text{H}_5\text{Br}$ gives a pentyne. The value of X is _____.

Archives

JEE ADVANCED

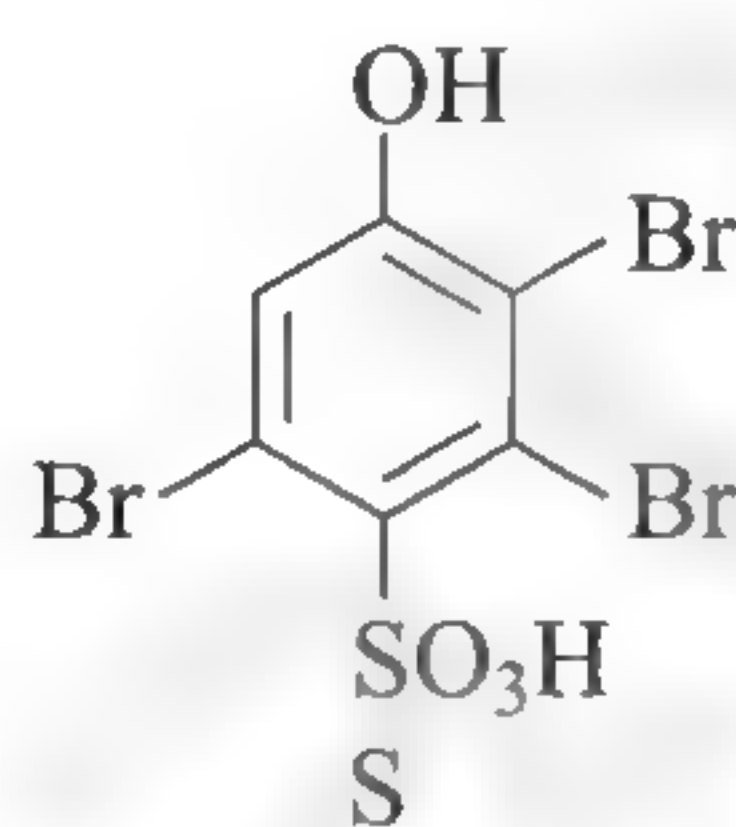
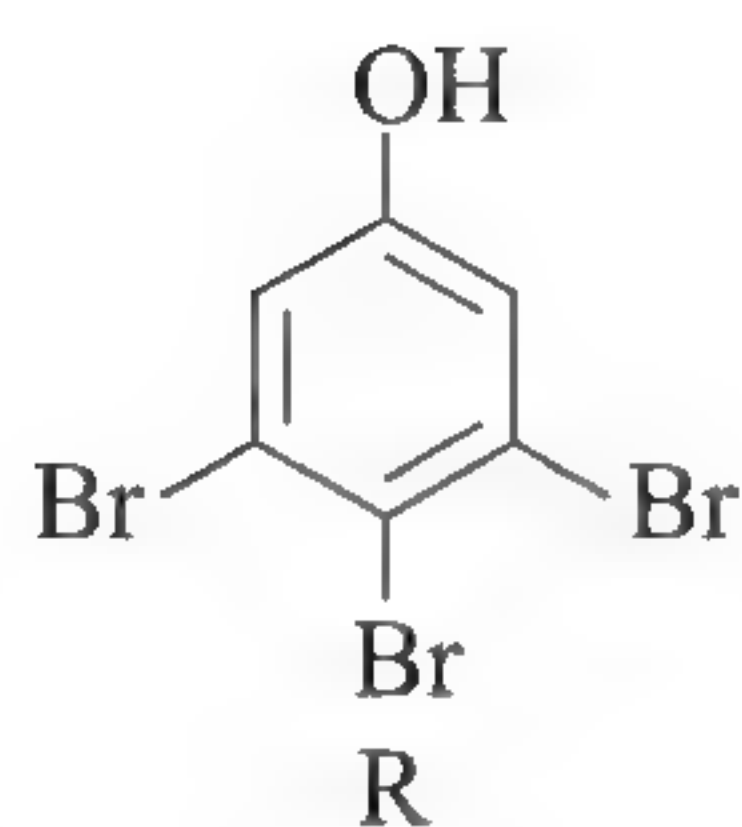
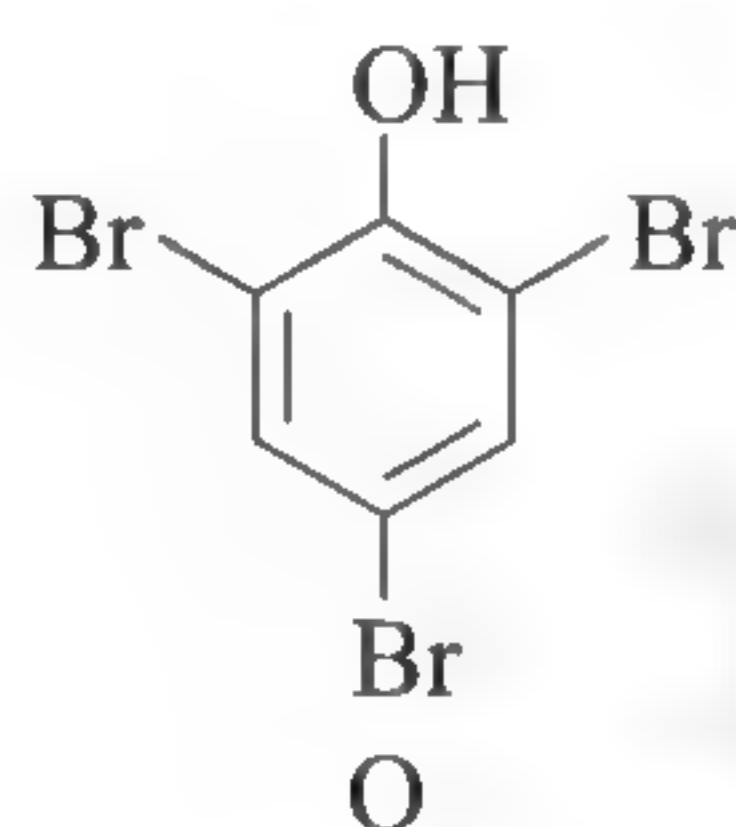
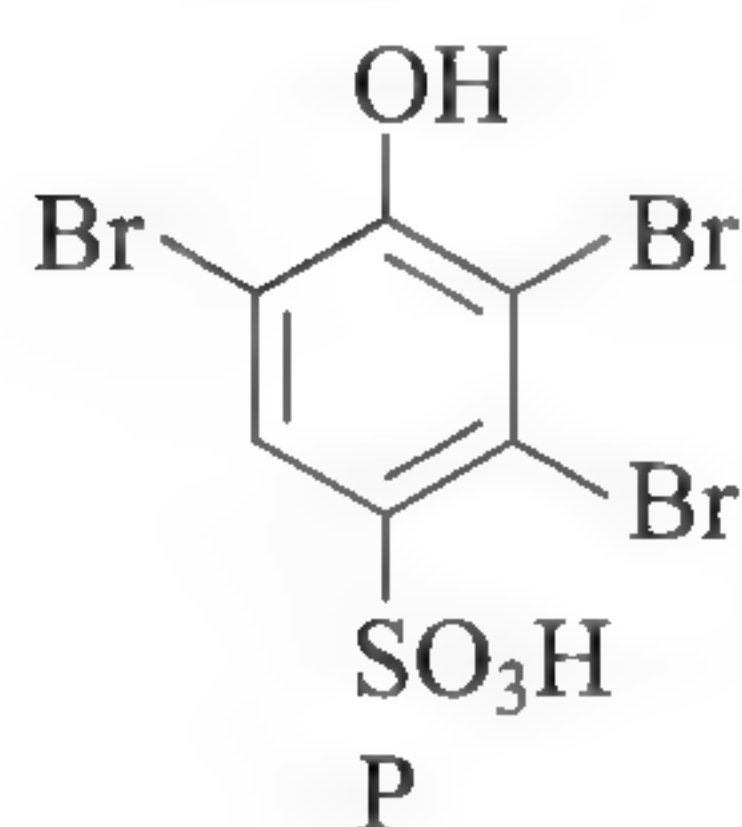
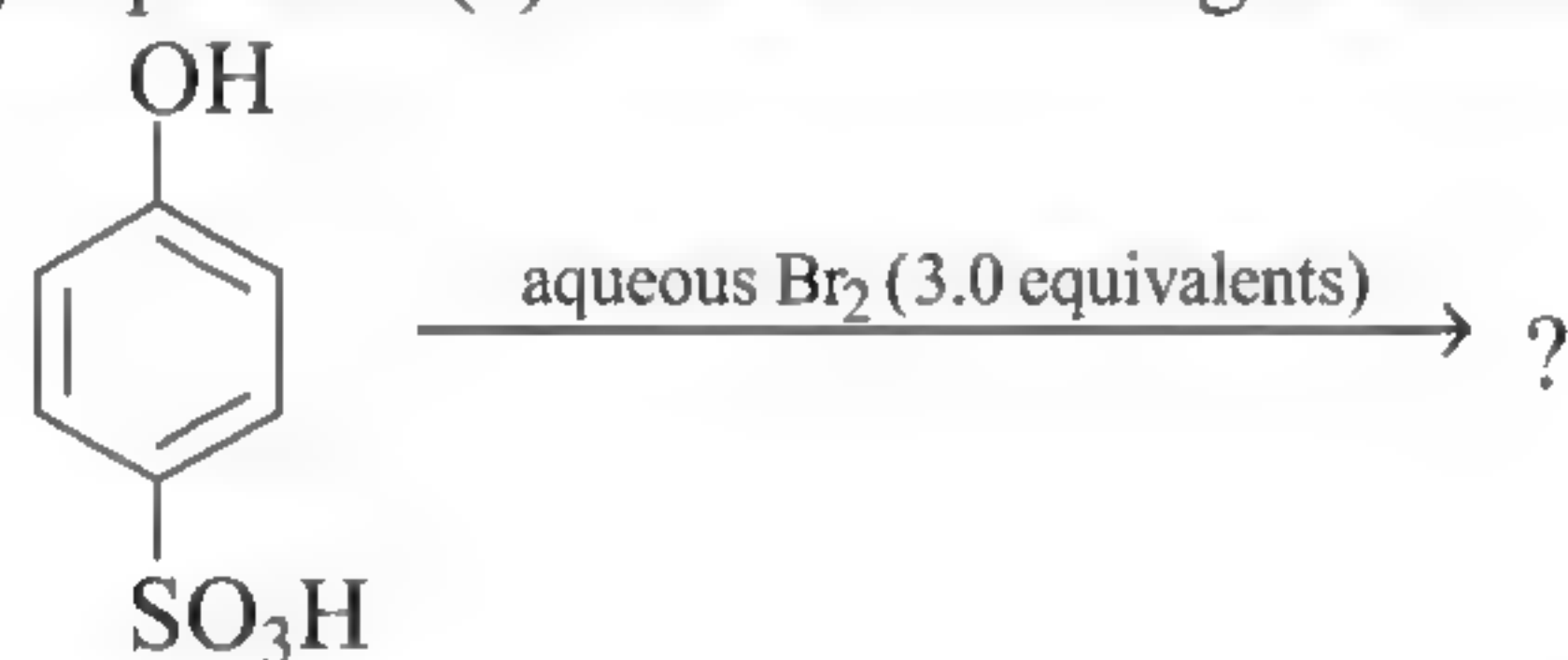
Single Correct Answer Type

1. Compound (A) C_8H_9Br gives a white precipitate when warmed with alcoholic $AgNO_3$. Oxidation of (A) gives an acid (B), $C_8H_6O_4$. (B) easily forms anhydride on heating. Identify the compound (A).



(IIT-JEE 2012)

2. The major product(s) of the following reaction is (are)



(1) P

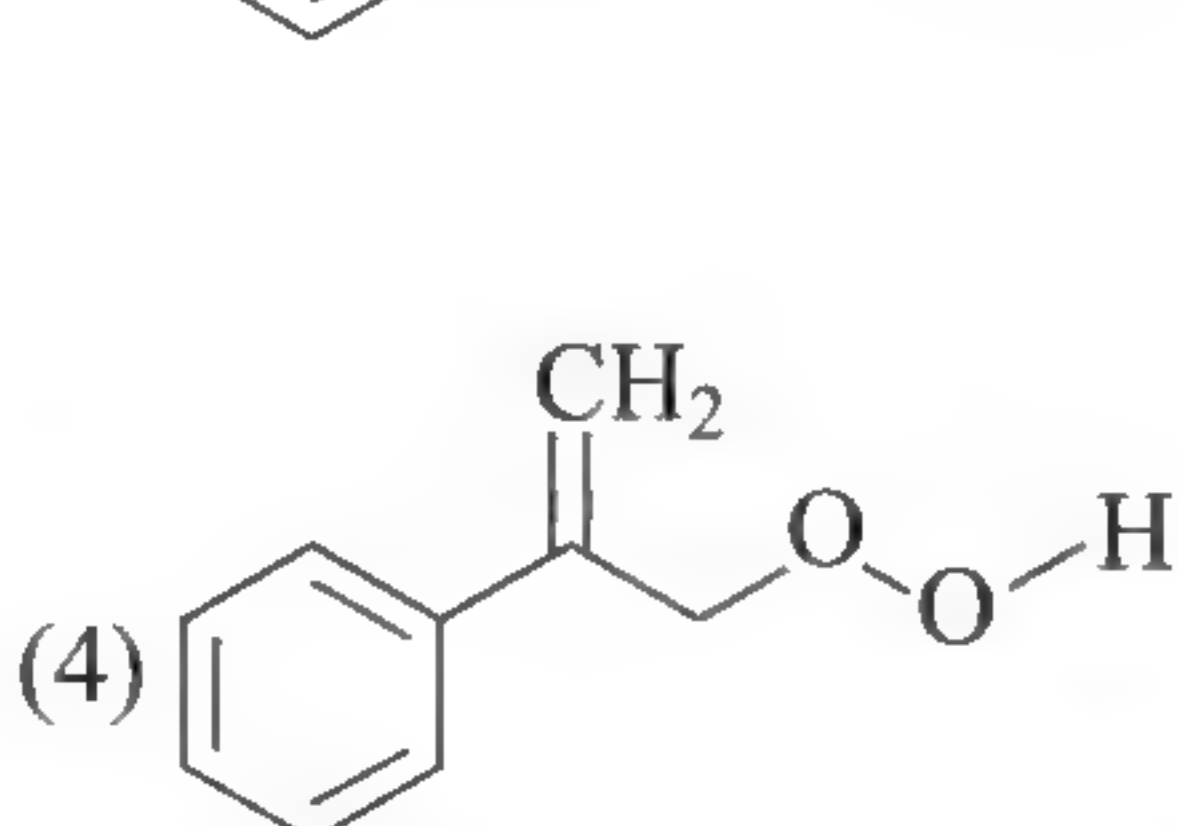
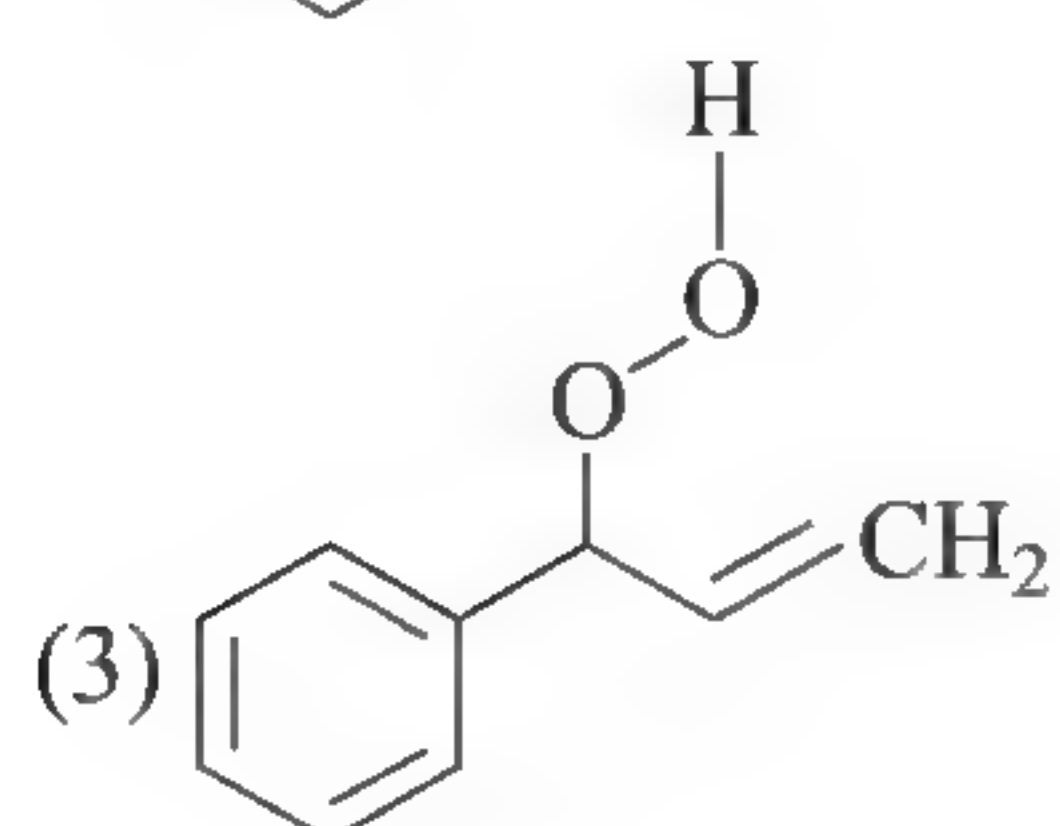
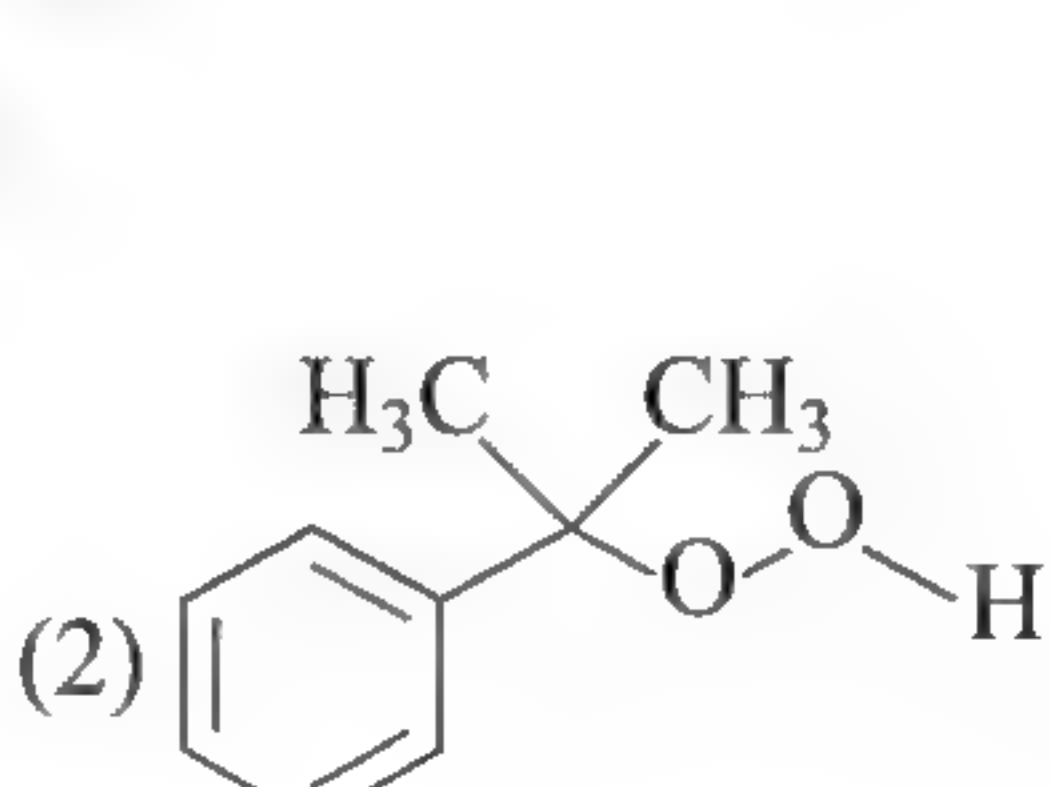
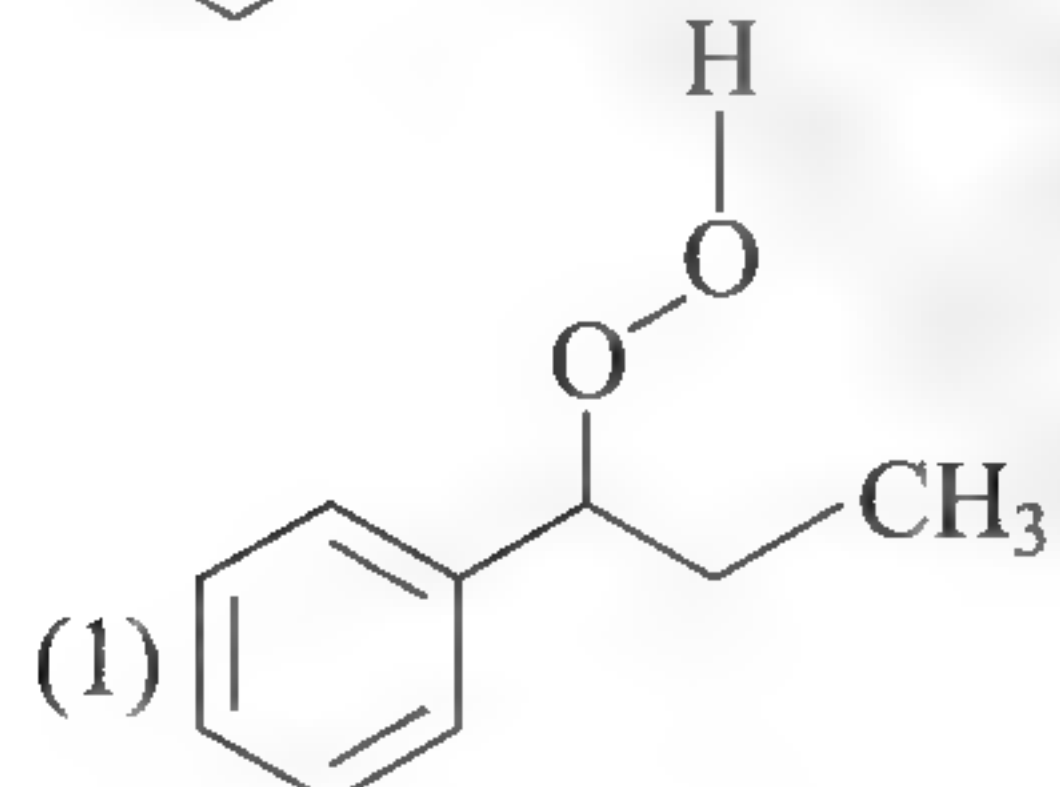
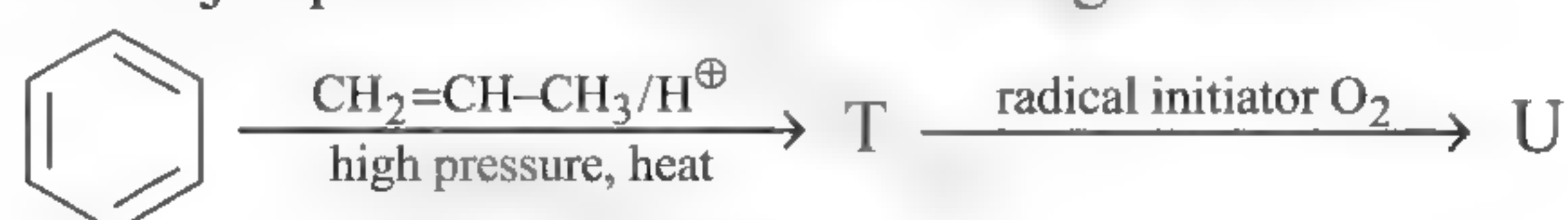
(2) Q

(3) R

(4) S

(JEE Advanced 2013)

3. The major product U in the following reaction is



(JEE Advanced 2015)

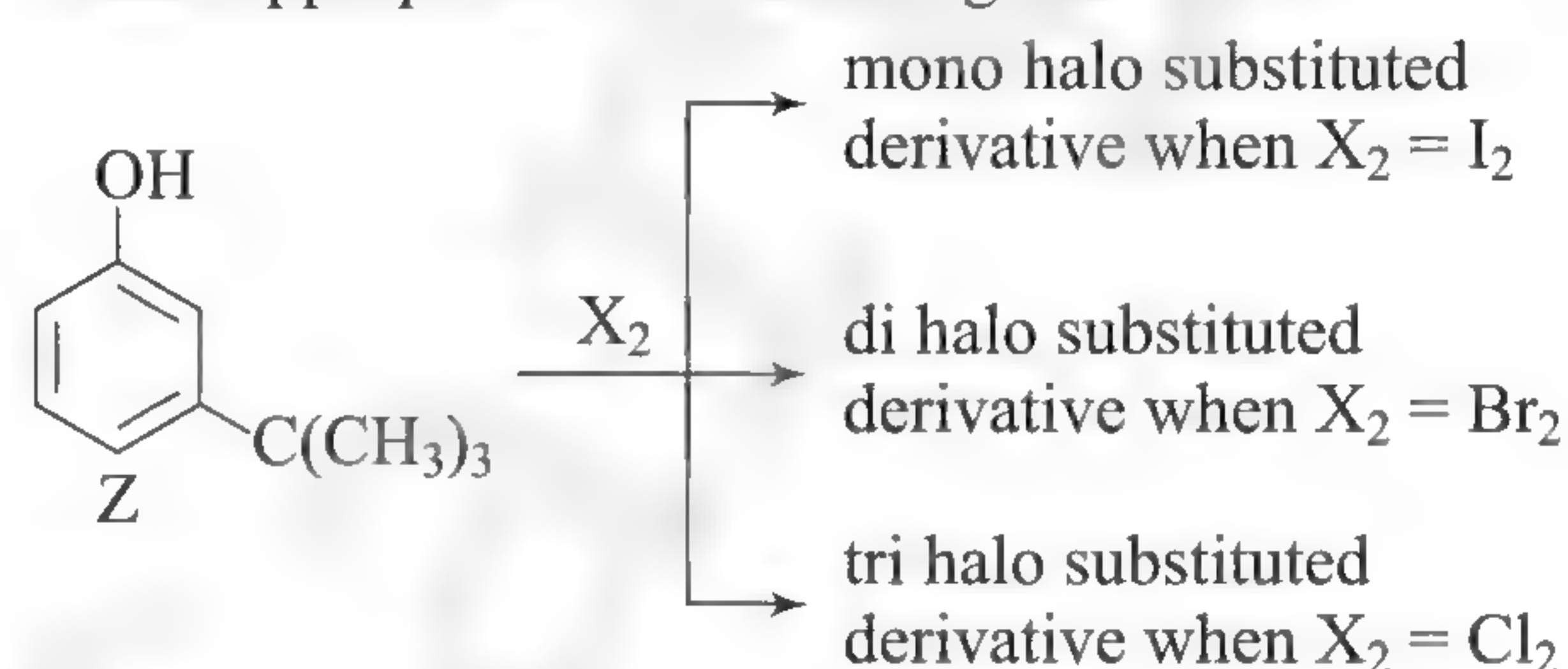
4. The synthesis of alkyl fluorides is best accomplished by:

- (1) Free radical fluorination (2) Sandmeyer's reaction
(3) Finkelstein reaction (4) Swarts reaction

(JEE Advanced 2015)

Multiple Correct Answers Type

1. The reactivity of compound Z with different halogens under appropriate conditions is given below:

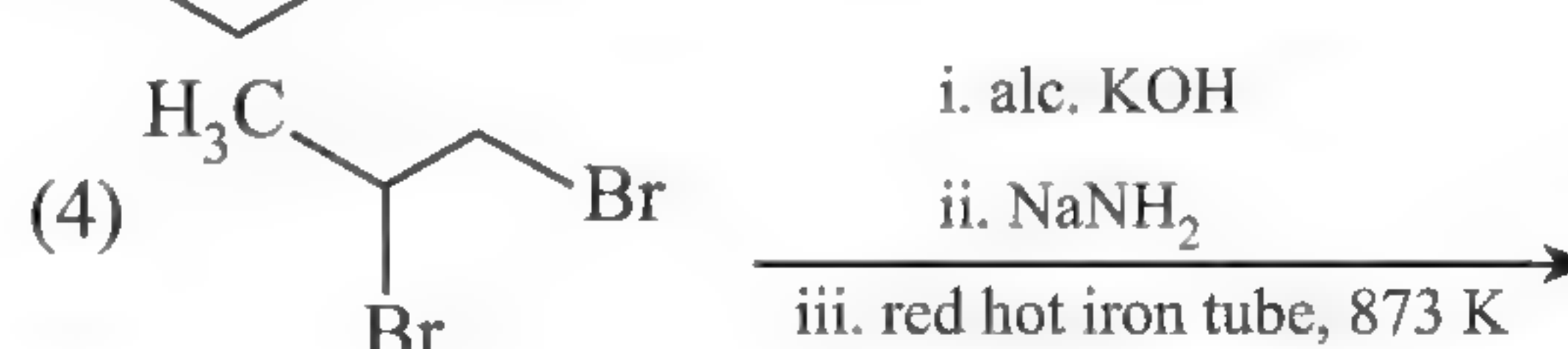
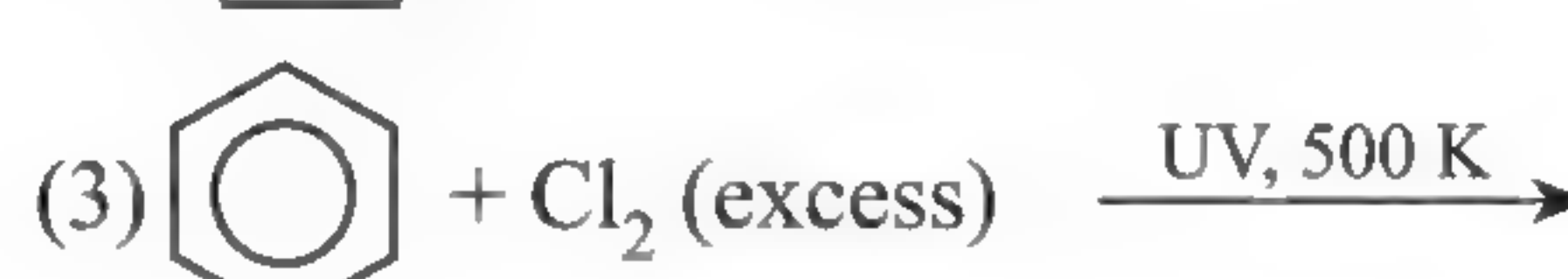
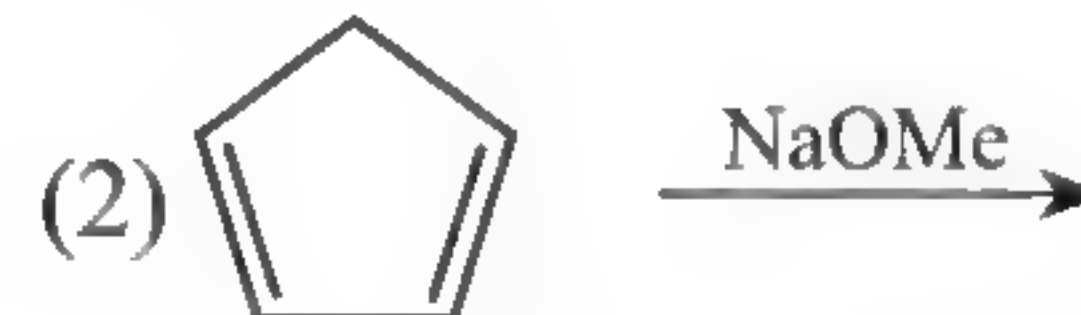
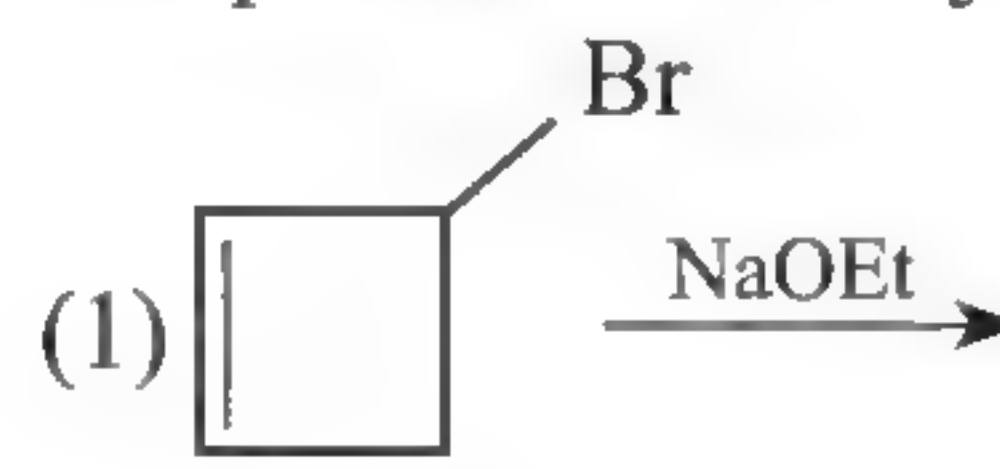


the observed pattern of electrophilic substitution can be explained by

- (1) the steric effect of the halogen
(2) the steric effect of the *tert*-butyl group
(3) the electronic effect of the phenolic group
(4) the electronic effect of the *tert*-butyl group

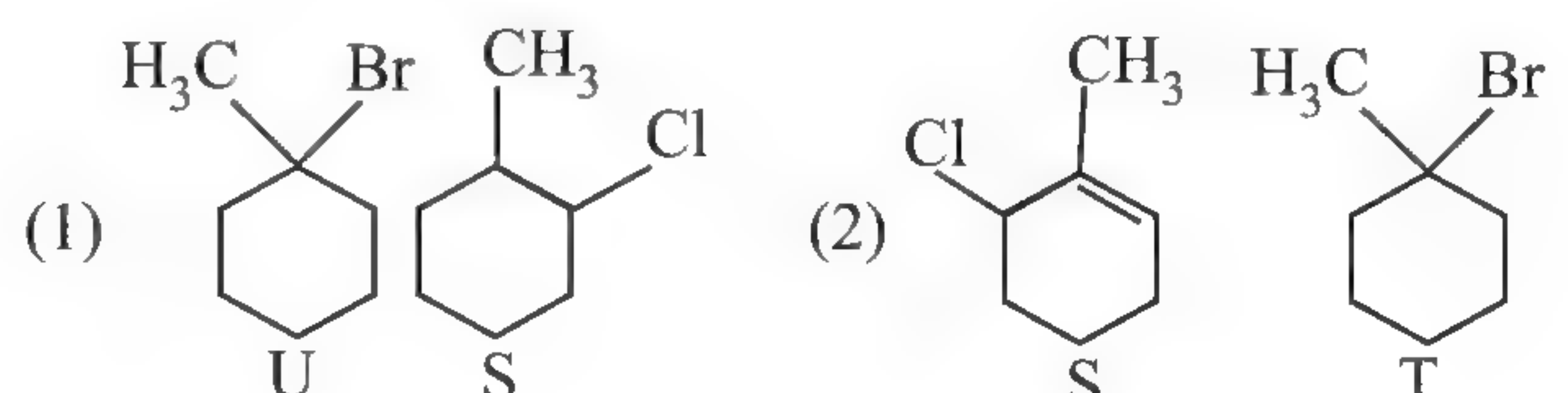
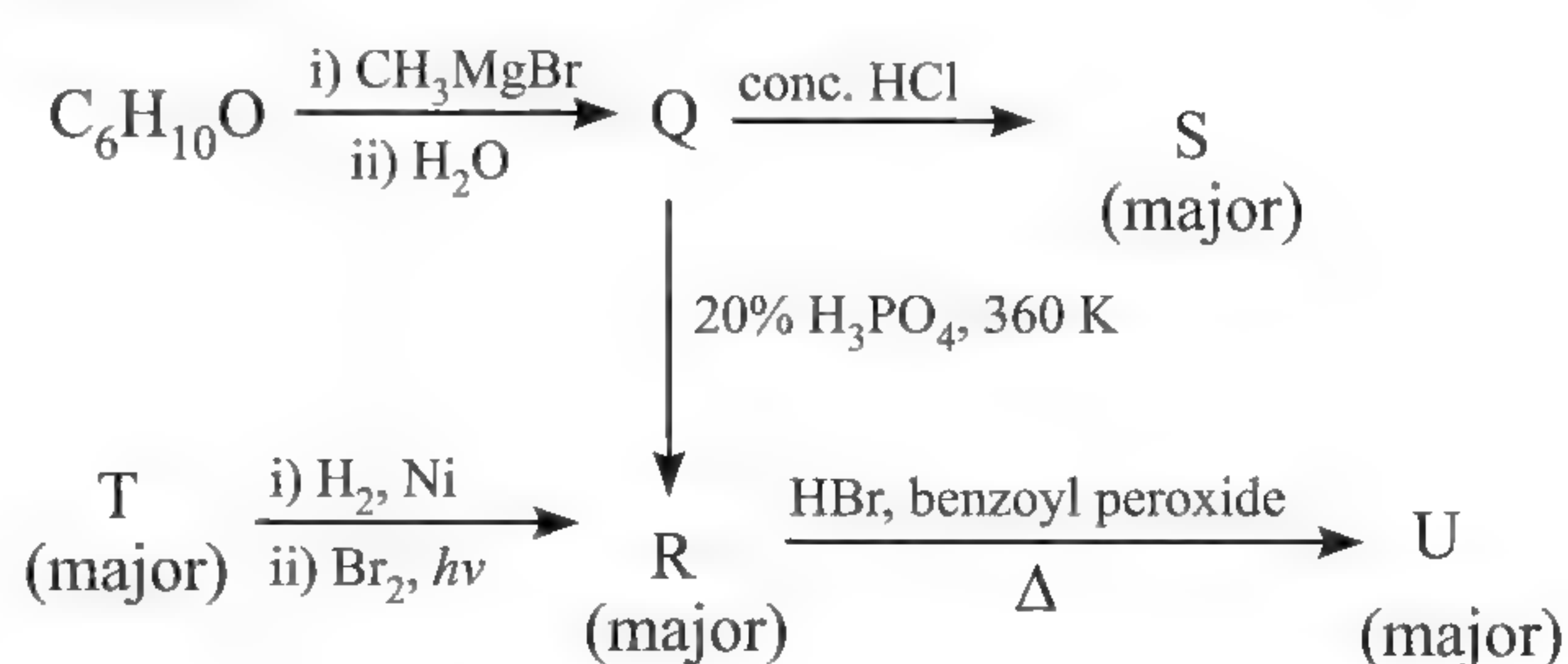
(JEE Advanced 2014)

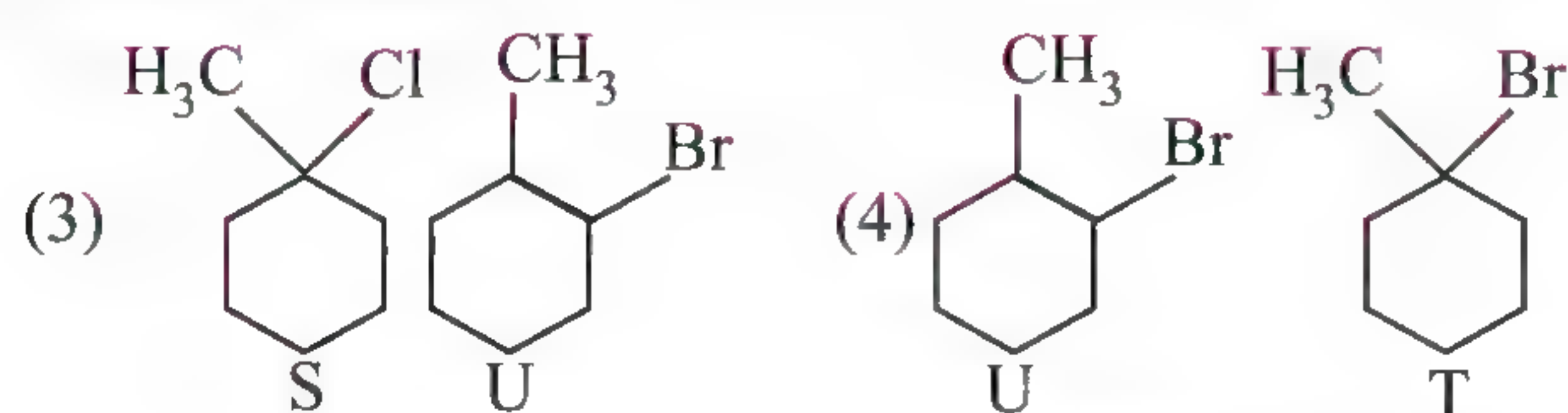
2. Choose the correct option(s) that give(s) an aromatic compound as the major product.



(JEE Advanced 2019)

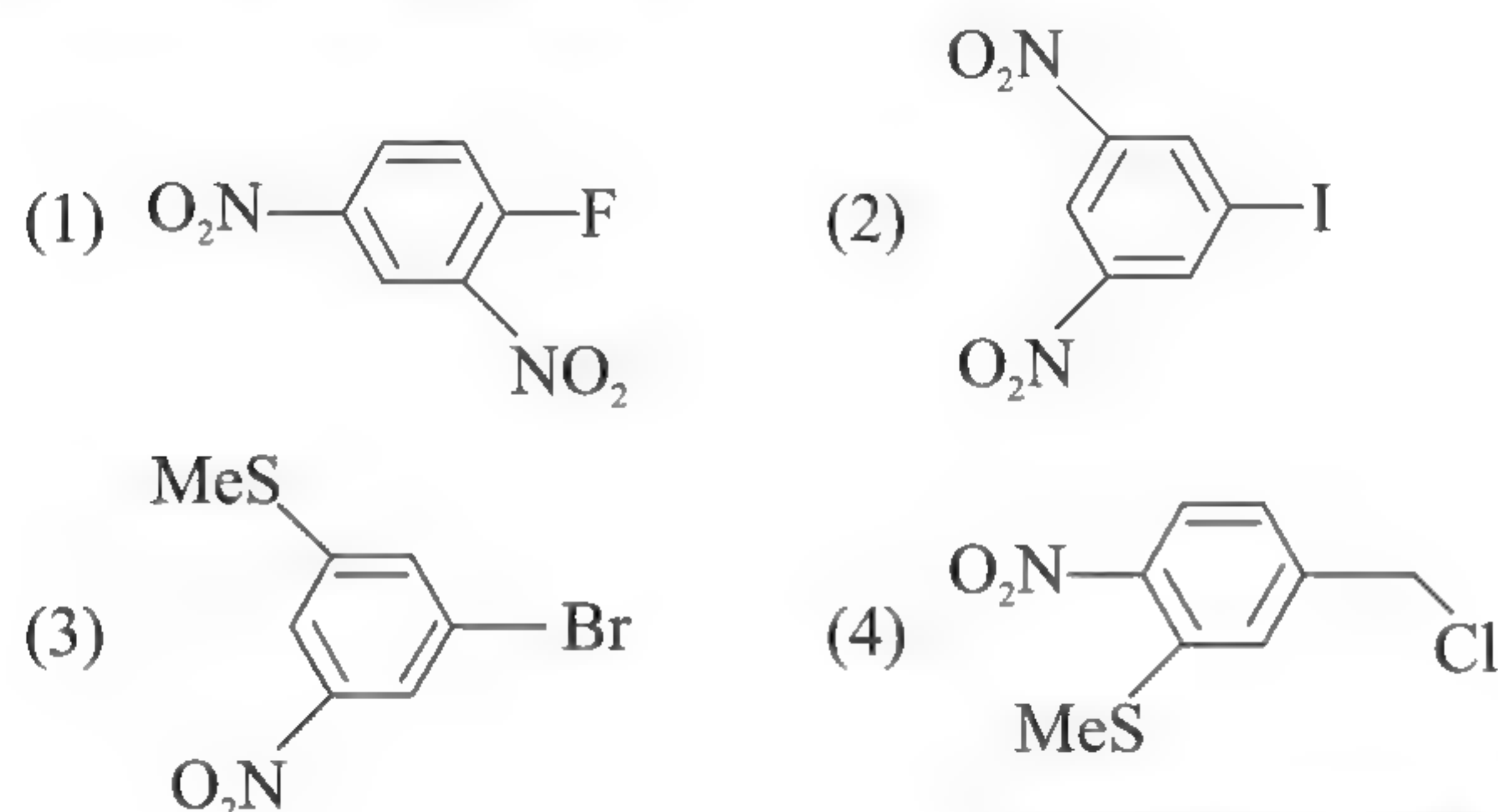
3. Choose the correct option(s) for the following set of reactions:





(JEE Advanced 2019)

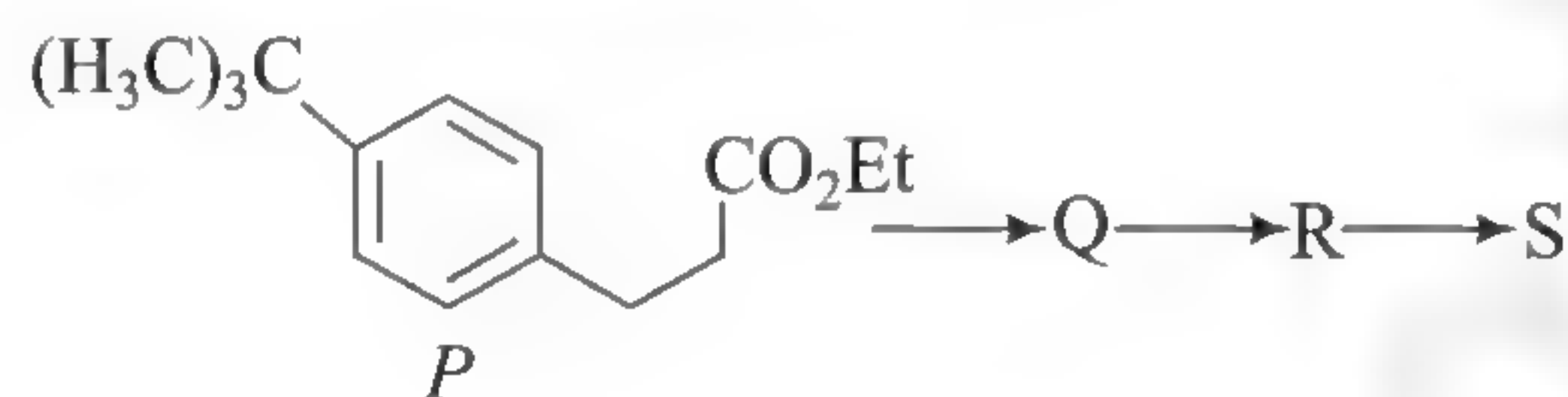
4. The reaction of *Q* with PhSNa yields an organic compound (major product) that gives positive Carius test on treatment with Na_2O_2 followed by addition of BaCl_2 . The correct option(s) for *Q* is (are)



(JEE Advanced 2021)

Linked Comprehension Type**For questions Q. 1 and Q. 2:**

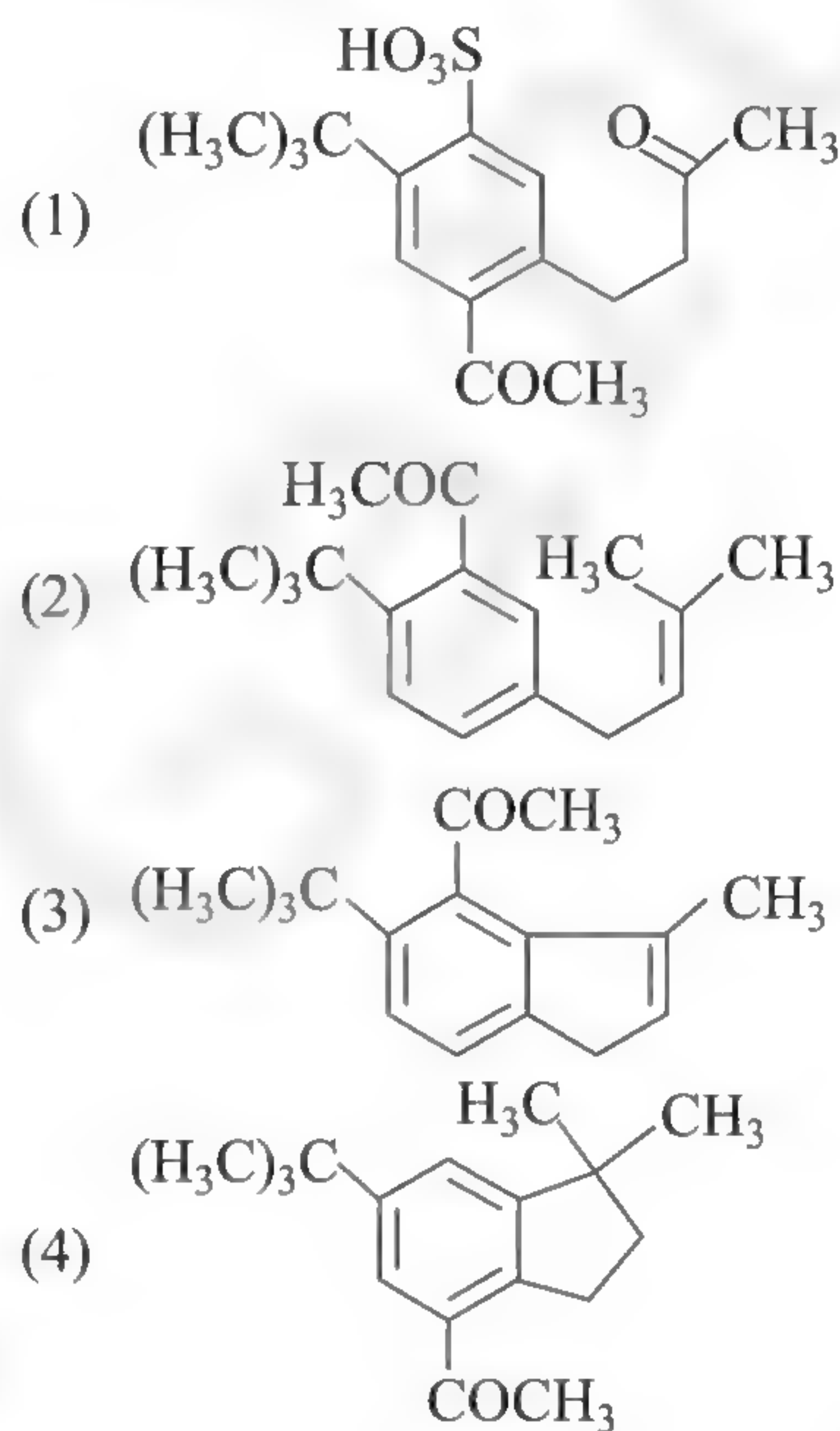
The reaction of compound *P* with CH_3MgBr (excess) in $(\text{C}_2\text{H}_5)_2\text{O}$ followed by addition of H_2O gives *Q*. The compound *Q* on treatment with H_2SO_4 at 0°C gives *R*. The reaction of *R* with CH_3COCl in the presence of anhydrous AlCl_3 in CH_2Cl_2 followed by treatment with H_2O produces compounds *S*.

[Et in compound *P* is ethyl group]

1. The reactions, *Q* to *R* and *R* to *S*, are

- (1) Dehydration and Friedel-Crafts acylation
- (2) Friedel-Crafts alkylation, dehydration and Friedel-Crafts acylation
- (3) Aromatic sulfonation and Friedel-Crafts acylation
- (4) Friedel-Crafts alkylation and Friedel-Crafts acylation

2. The product *S* is



(JEE Advanced 2017)

Answers Key

EXERCISES

Single Correct Answer Type

- | | | | | |
|----------|----------|----------|----------|----------|
| 1. (3) | 2. (3) | 3. (2) | 4. (3) | 5. (2) |
| 6. (3) | 7. (4) | 8. (4) | 9. (2) | 10. (3) |
| 11. (2) | 12. (2) | 13. (2) | 14. (3) | 15. (3) |
| 16. (4) | 17. (3) | 18. (1) | 19. (2) | 20. (2) |
| 21. (2) | 22. (2) | 23. (2) | 24. (4) | 25. (4) |
| 26. (4) | 27. (3) | 28. (3) | 29. (4) | 30. (1) |
| 31. (3) | 32. (4) | 33. (2) | 34. (1) | 35. (4) |
| 36. (3) | 37. (1) | 38. (3) | 39. (4) | 40. (4) |
| 41. (3) | 42. (1) | 43. (3) | 44. (1) | 45. (3) |
| 46. (2) | 47. (3) | 48. (4) | 49. (2) | 50. (1) |
| 51. (3) | 52. (3) | 53. (1) | 54. (4) | 55. (2) |
| 56. (4) | 57. (4) | 58. (1) | 59. (2) | 60. (1) |
| 61. (1) | 62. (1) | 63. (4) | 64. (1) | 65. (1) |
| 66. (4) | 67. (3) | 68. (3) | 69. (2) | 70. (3) |
| 71. (2) | 72. (3) | 73. (4) | 74. (1) | 75. (2) |
| 76. (1) | 77. (2) | 78. (2) | 79. (3) | 80. (2) |
| 81. (2) | 82. (2) | 83. (1) | 84. (3) | 85. (1) |
| 86. (3) | 87. (1) | 88. (4) | 89. (3) | 90. (4) |
| 91. (1) | 92. (2) | 93. (2) | 94. (2) | 95. (4) |
| 96. (3) | 97. (4) | 98. (1) | 99. (2) | 100. (2) |
| 101. (2) | 102. (1) | 103. (2) | 104. (4) | 105. (3) |
| 106. (2) | 107. (1) | 108. (4) | 109. (3) | 110. (2) |
| 111. (4) | 112. (1) | 113. (4) | 114. (4) | 115. (1) |
| 116. (3) | 117. (1) | 118. (1) | 119. (4) | 120. (1) |
| 121. (4) | 122. (1) | 123. (3) | 124. (2) | 125. (1) |
| 126. (3) | 127. (1) | 128. (3) | 129. (2) | 130. (1) |
| 131. (2) | 132. (3) | 133. (1) | 134. (2) | 135. (2) |
| 136. (1) | 137. (2) | 138. (2) | 139. (1) | 140. (1) |
| 141. (2) | 142. (3) | 143. (3) | 144. (4) | 145. (1) |
| 146. (2) | 147. (2) | 148. (1) | 149. (1) | 150. (2) |
| 151. (1) | 152. (1) | 153. (2) | 154. (3) | 155. (3) |
| 156. (4) | 157. (1) | 158. (1) | 159. (2) | 160. (2) |
| 161. (4) | 162. (3) | | | |

Multiple Correct Answers Type

- | | | |
|------------------|---------------|---------------|
| 1. (1), (2) | 2. (1) | 3. (1, 3, 4) |
| 4. (1, 3) | 5. (1, 2, 3) | 6. (1, 2) |
| 7. (1, 2, 3) | 8. (1, 2, 3) | 9. (1, 2, 3) |
| 10. (1, 2, 3) | 11. (1, 2, 3) | 12. (1, 4) |
| 13. (1, 2, 3) | 14. (4) | 15. (1, 3, 4) |
| 16. (1, 2, 3, 4) | 17. (1, 2, 3) | 18. (1, 2, 3) |
| 19. (2, 3, 4) | | |

Linked Comprehension Type

- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (1) | 2. (3) | 3. (2) | 4. (2) | 5. (2) |
| 6. (1) | 7. (4) | 8. (2) | 9. (2) | 10. (3) |
| 11. (1) | 12. (4) | 13. (2) | 14. (4) | 15. (1) |
| 16. (3) | 17. (1) | 18. (2) | 19. (3) | 20. (2) |
| 21. (3) | 22. (1) | 23. (1) | 24. (2) | 25. (3) |

Matrix Match Type

- (a \rightarrow q, r; b \rightarrow t; c \rightarrow p, q, s; d \rightarrow q, t)
- (a. \rightarrow p, r; b. \rightarrow p, r; c. \rightarrow p, s; d. \rightarrow q, r)
- (a. \rightarrow p, r; b. \rightarrow p, r; c. \rightarrow q; d. \rightarrow p)
- (a—iii—p; b—iv—s; c—i—q, t; d—ii—r)
- (a \rightarrow r; b \rightarrow s; c \rightarrow t; d \rightarrow u, e \rightarrow v; f. \rightarrow p; g \rightarrow q)
- (a \rightarrow p, q, s; b \rightarrow p, q, r, s; c \rightarrow q, r, s)
- (a \rightarrow r, s; b \rightarrow p; c \rightarrow t; d \rightarrow q; e \rightarrow u)

Numerical Value Type

- | | | | | |
|--------|--------|--------|--------|---------|
| 1. (8) | 2. (8) | 3. (9) | 4. (2) | 5. (1) |
| 6. (3) | 7. (1) | 8. (5) | 9. (4) | 10. (3) |

ARCHIVES

JEE Advanced

Single Correct Answer Type

- | | | | |
|--------|--------|--------|--------|
| 1. (3) | 2. (2) | 3. (2) | 4. (4) |
|--------|--------|--------|--------|

Multiple Correct Answers Type

- | | | |
|--------------|-----------|-----------|
| 1. (1, 2, 3) | 2. (2, 4) | 3. (3, 4) |
| 4. (1, 4) | | |

Linked Comprehension Type

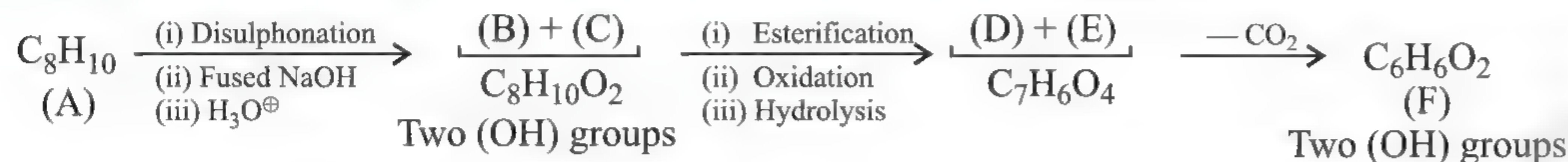
- | | |
|--------|--------|
| 1. (2) | 2. (4) |
|--------|--------|

Chapter 3

Concept Application Exercises

Exercise 3.1

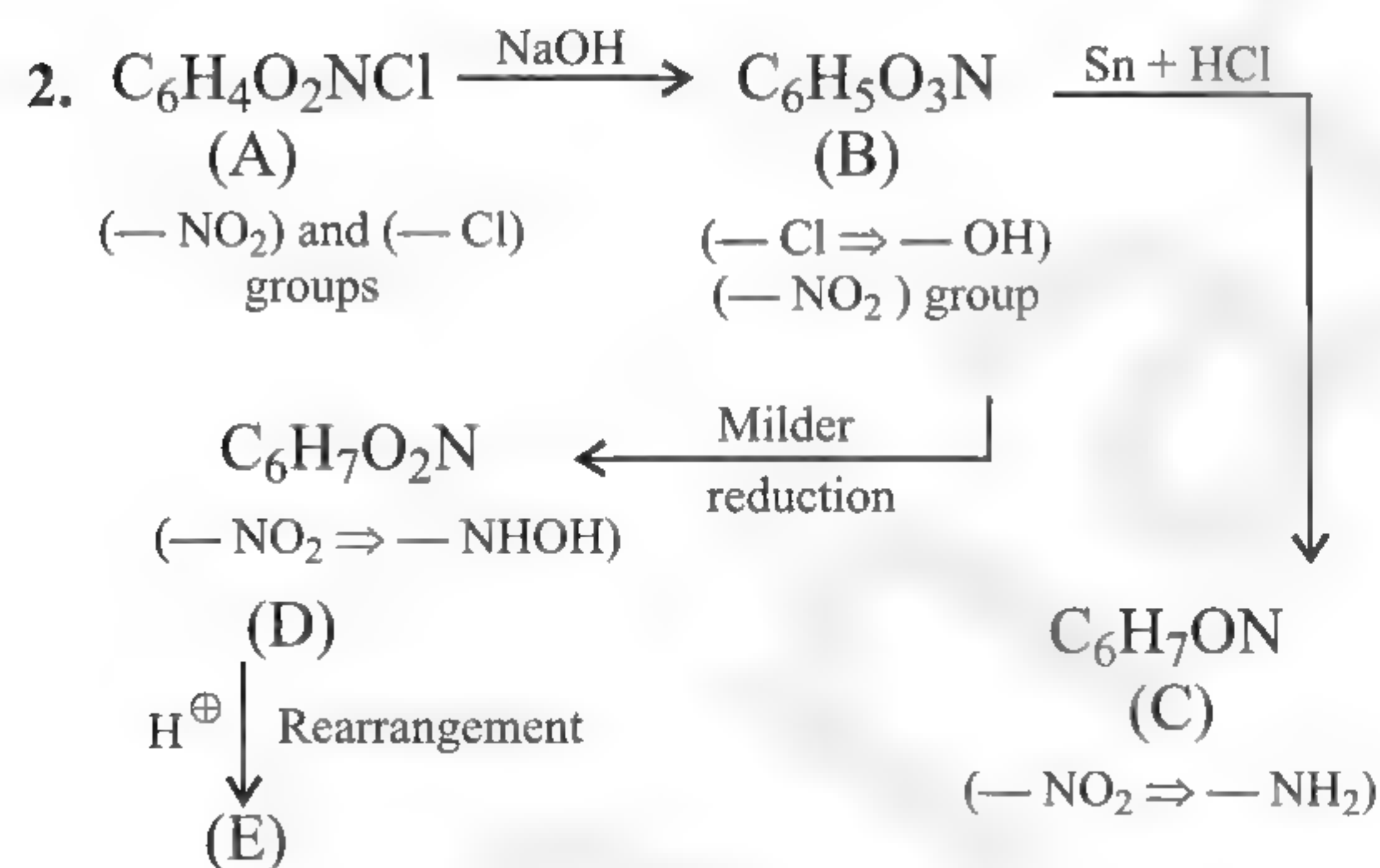
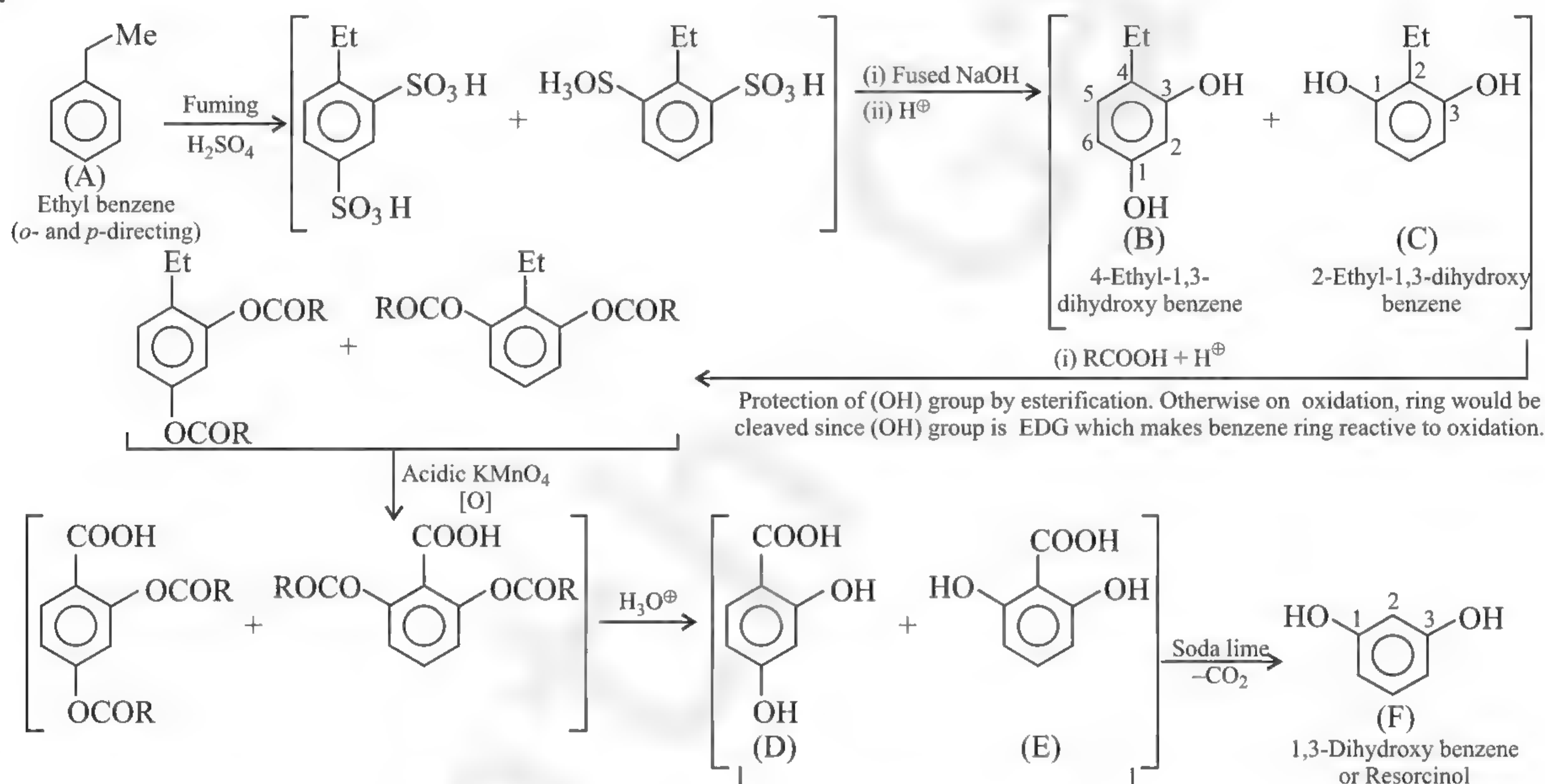
1. 4 D.U. and C:H \approx 1:1 in (A) suggest benzene ring with either two (Me) groups in the ring or one (Et) group in the side chain.



Formation of (F) suggests that only one (–COOH) is decarboxylated because from the above reaction sequence it is clear that (F) contains two (OH) groups.

Therefore, (A) contains (Et) group.

Reactions:

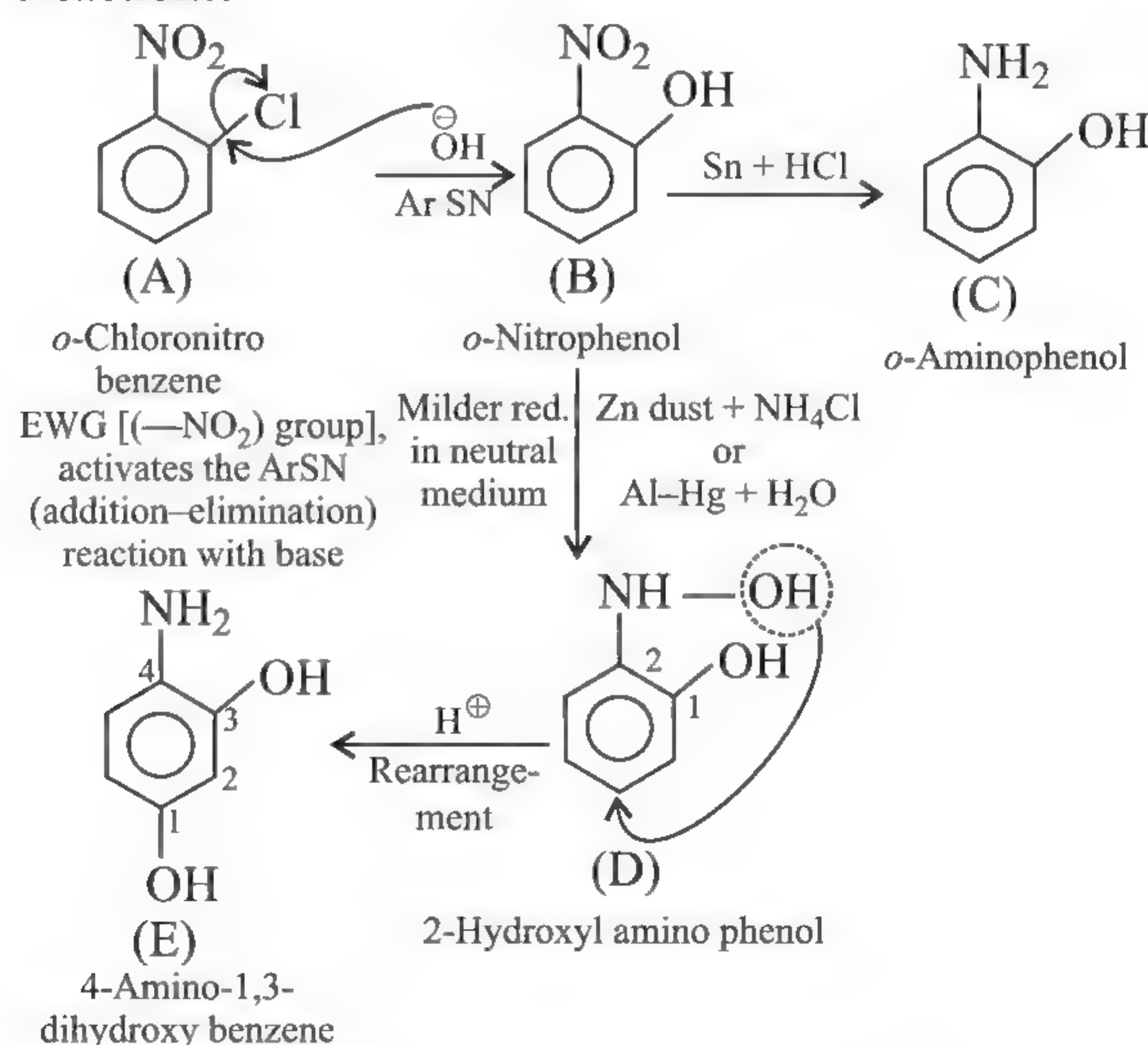


(D) to (E) formation shows rearrangement of (–NHOH) group in which (OH) group from (NHOH) migrates to p-position. So p-position is vacant. Therefore, (–NO₂) and (Cl) groups in (A) must be present at ortho-positions.

$$\begin{aligned} \text{D.U. in A} &= \frac{(2n_{\text{C}} + 2) + n_{\text{Cl}} - n_{\text{N}} - n_{\text{H}}}{2} \\ &= \frac{(2 \times 6 + 2) + 1 - 1 - 4}{2} = 5^{\circ} \end{aligned}$$

5 D.U. in (A) suggests benzene ring with 4 D.U. in benzene and 1 D.U. in (NO₂) group. (–NO₂) and (–Cl) groups are at ortho-position.

Reactions:

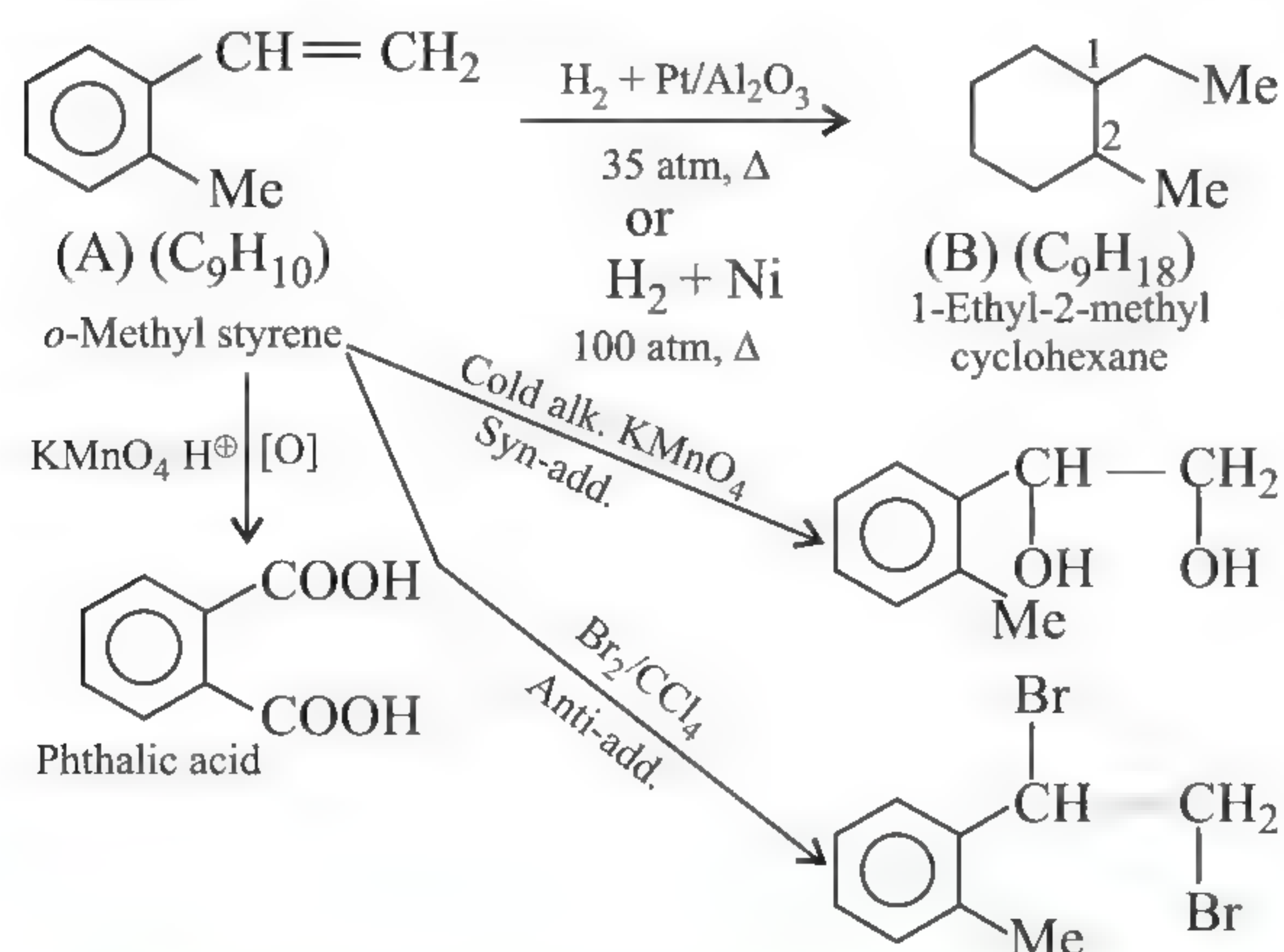


$$3. \text{D.U. in A} = \frac{(2n_{\text{C}} + 2) - n_{\text{H}}}{2} = \frac{(9 \times 2 + 2) - 10}{2} = 5^{\circ}$$

5 D.U. suggests benzene ring with one (C=C) bond in the side chain. The presence of double bond is shown by decolourisation of cold alk. KMnO₄ solution and reaction with Br₂.

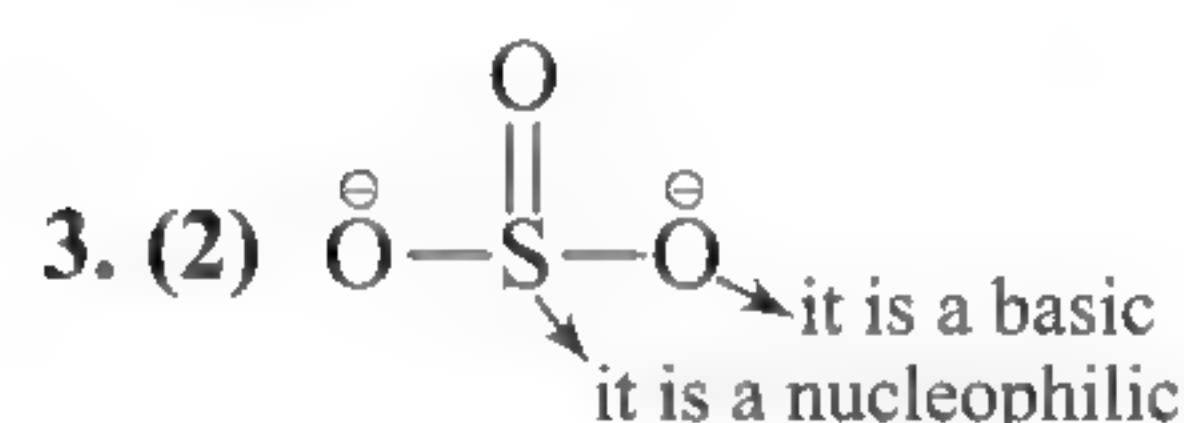
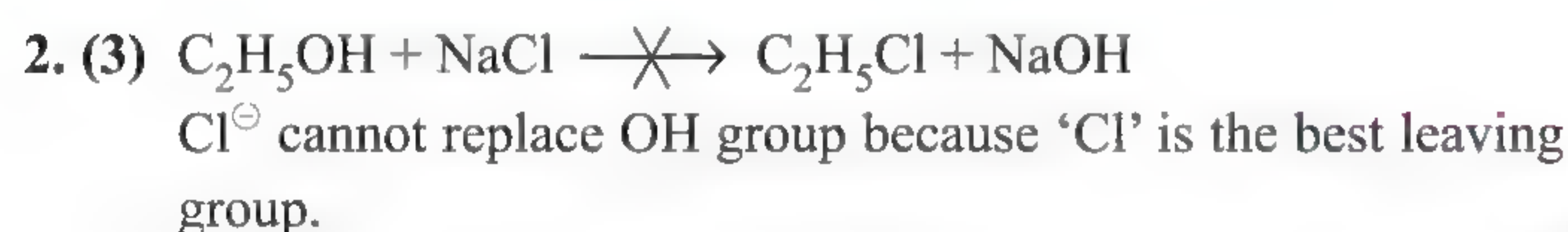
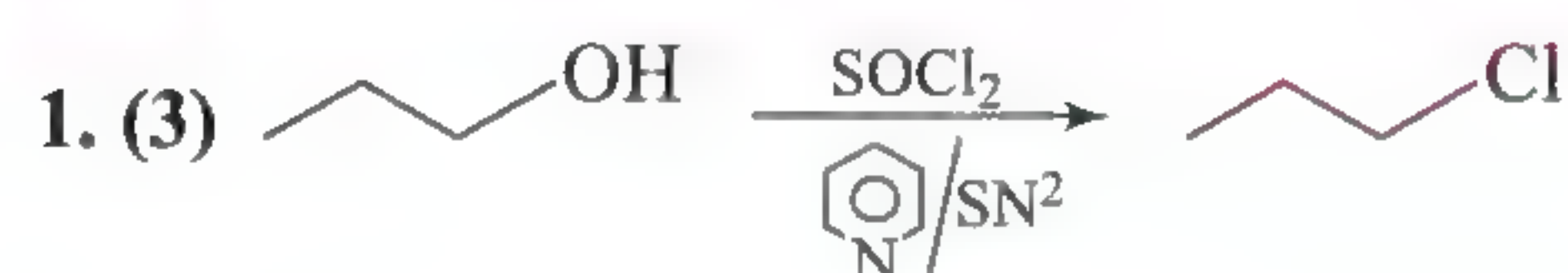
Oxidation of (A) to phthalic acid suggests that one (Me) group and ($\text{CH}_2=\text{CH}-$) group are at ortho-position.

Reactions:



Exercises

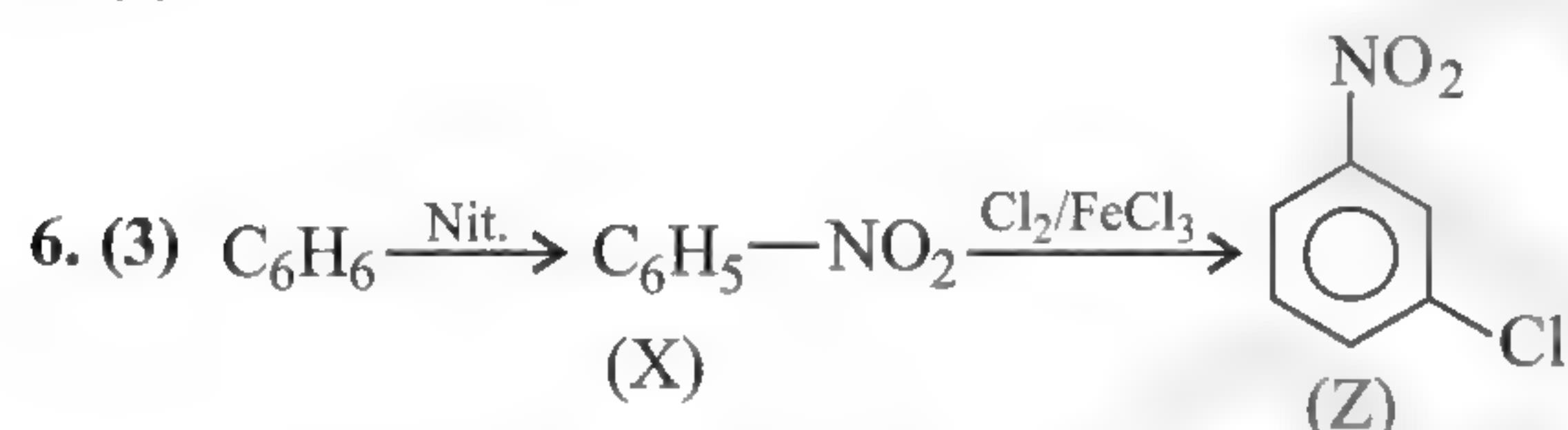
Single Correct Answer Type



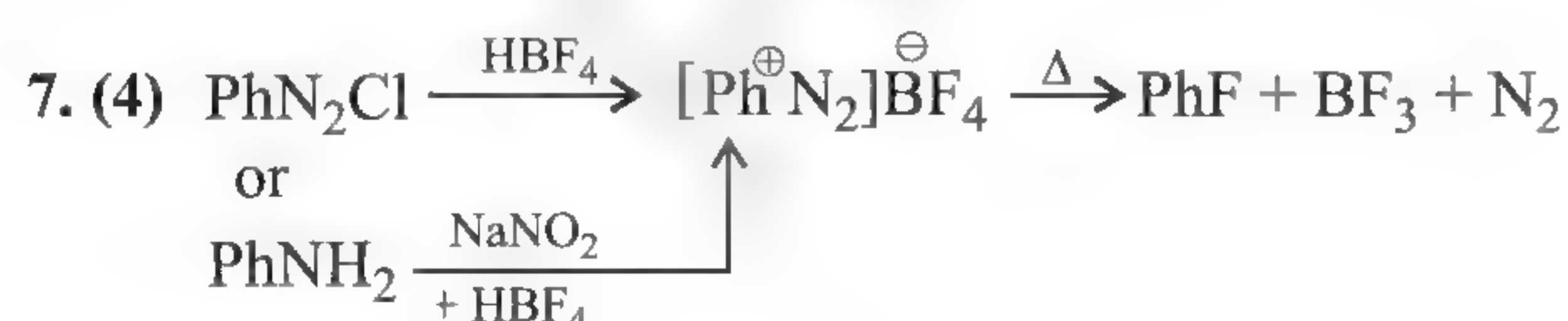
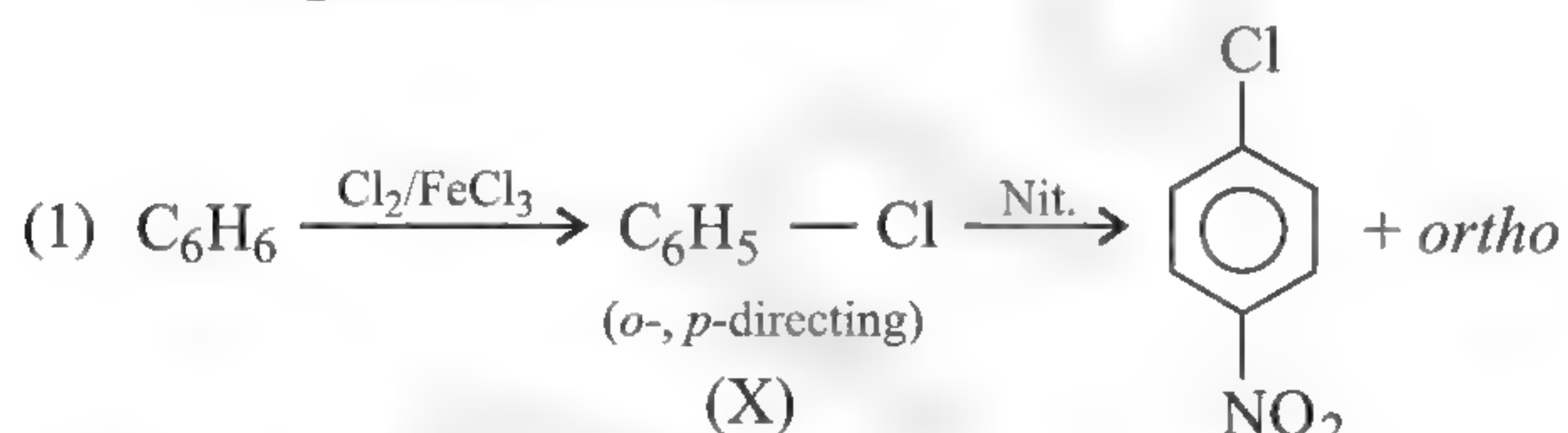
(Sulphur is better nucleophile than oxygen.) (But oxygen is better base than sulphur)

4. (3)

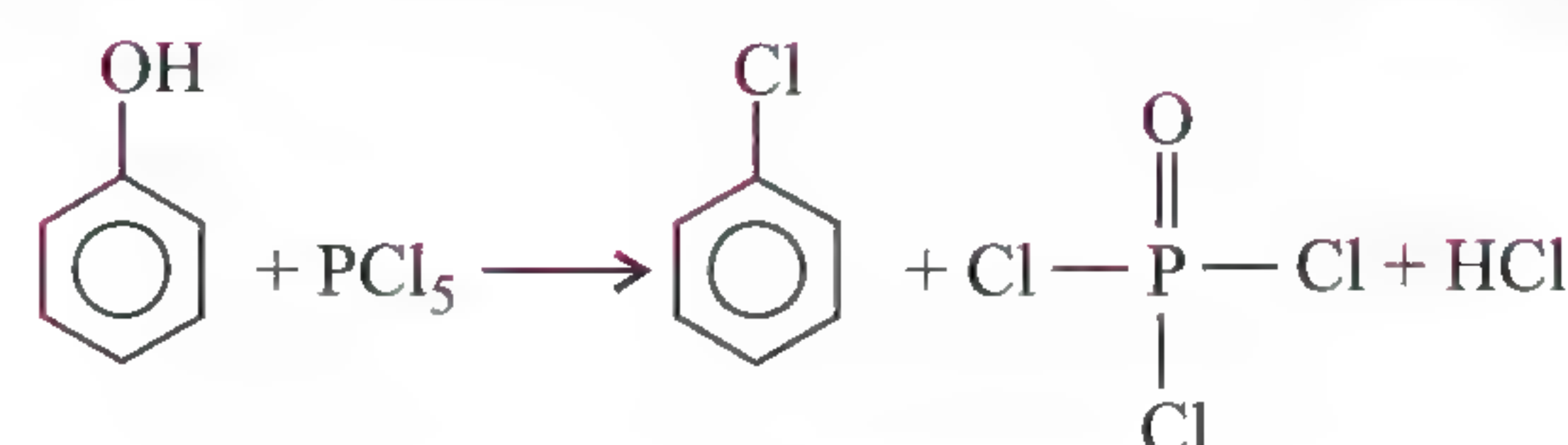
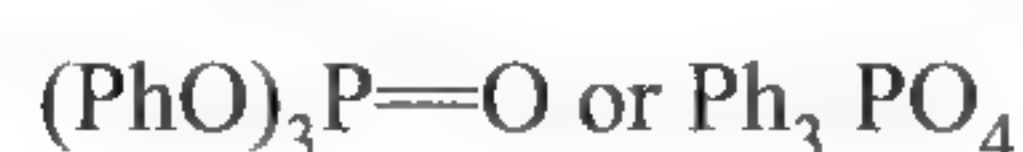
5. (2)



($-\text{NO}_2$) group is *m*-directing

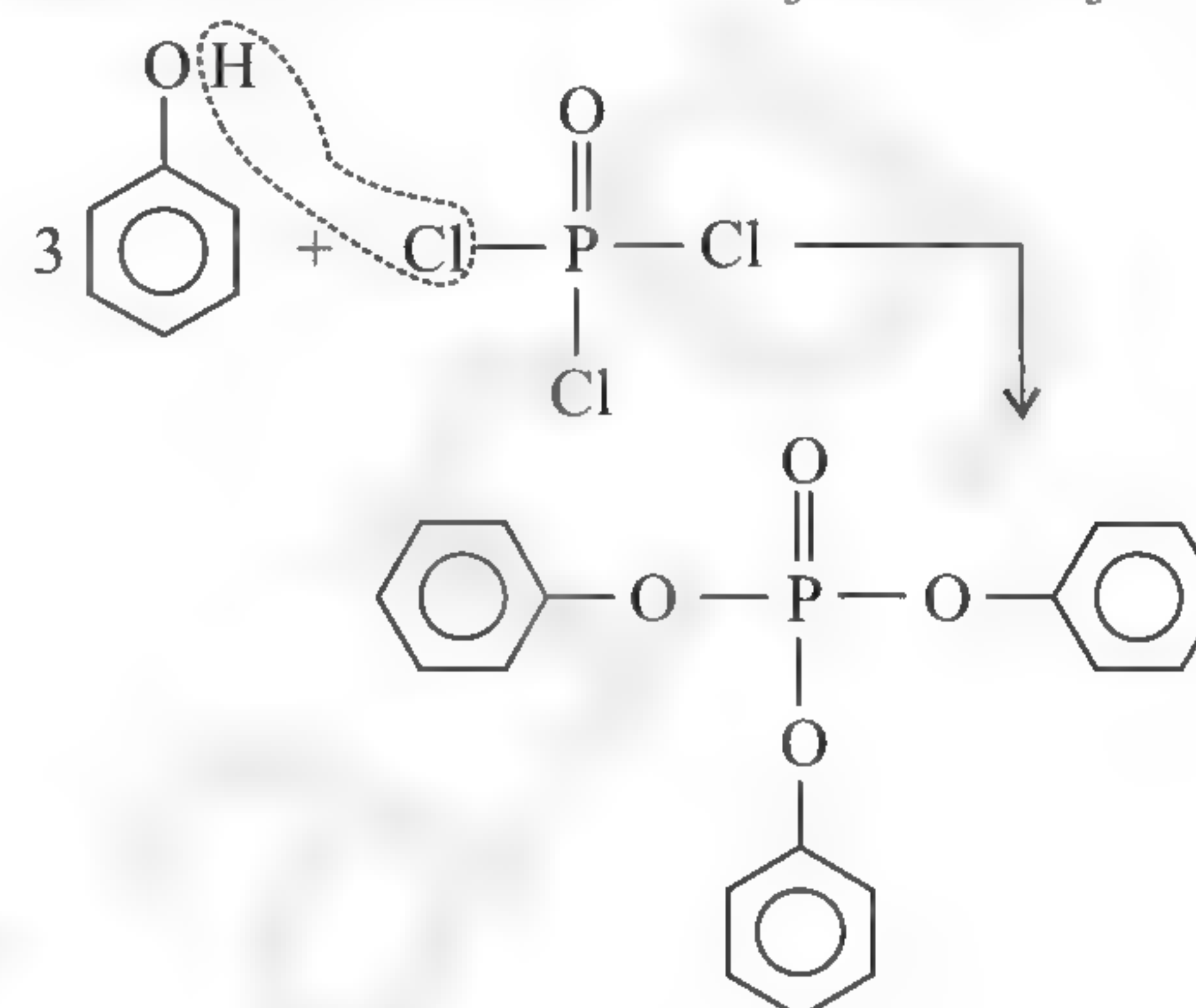


8. (4) The ($-\text{OH}$) group of phenol, unlike that of alcohol, is difficult to replace by a halogen, e.g., halogen acids have no action, and PX_3 yields only phosphorous esters. Phenol reacts with PCl_5 or PBr_5 , when the ($-\text{OH}$) group of phenol is replaced by a halogen atom. The yield of chloro or bromo benzene is small, the main product is triphenyl phosphate.

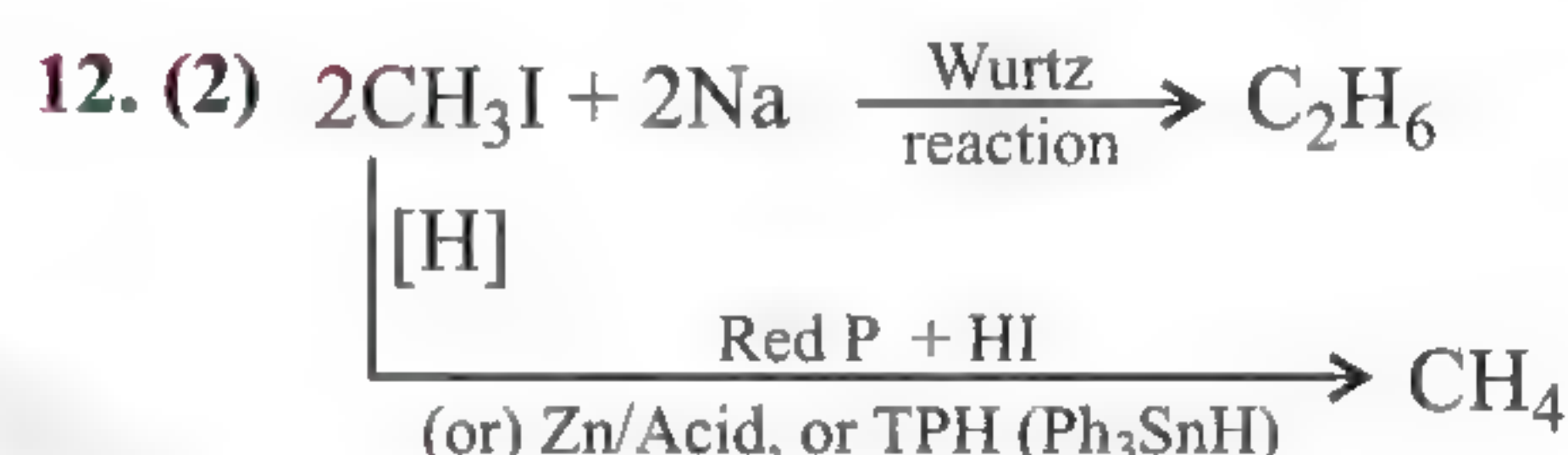
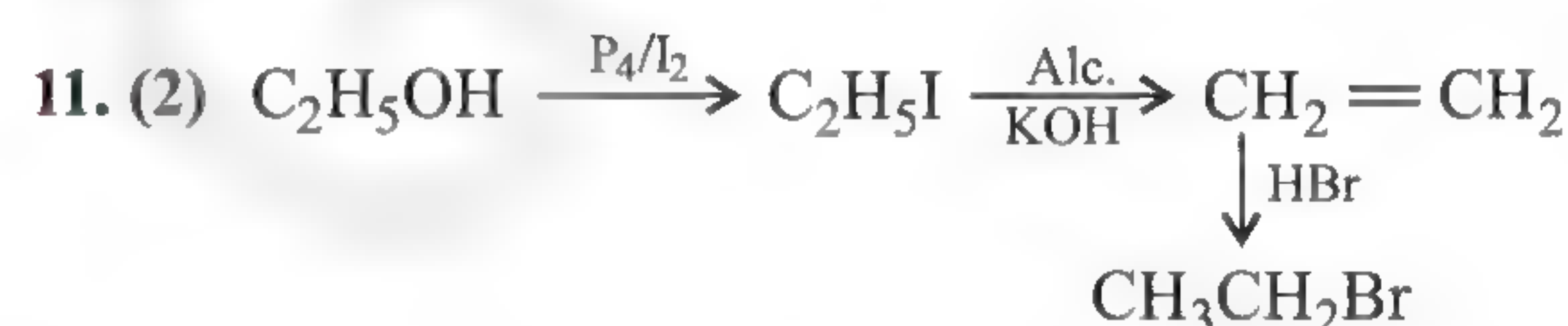


Small yield

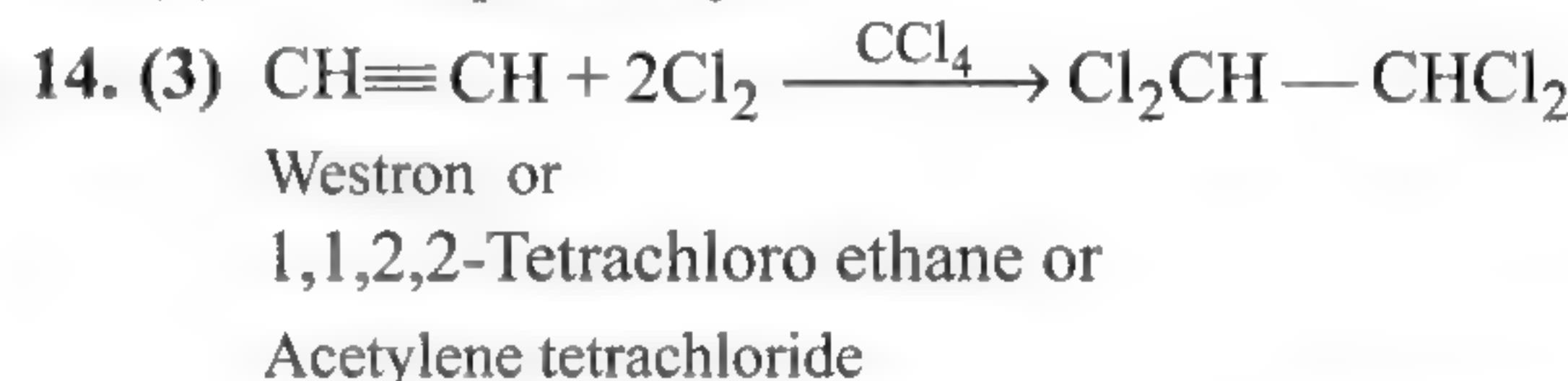
Phenol further reacts with POCl_3 to give Ph_3PO_4



9. (2) 10. (3)



13. (2) Self-explanatory.



Westron is used as an industrial solvent for rubber, fats, and varnishes. It has some insecticidal action.

15. (3) Chlorofluoro carbons are called Freon. CCl_2F_2 (Freon-12)

16. (4) When westron vapours are passed over heated BaCl_2 or lime, westrosol (trichloro ethylene) is obtained.

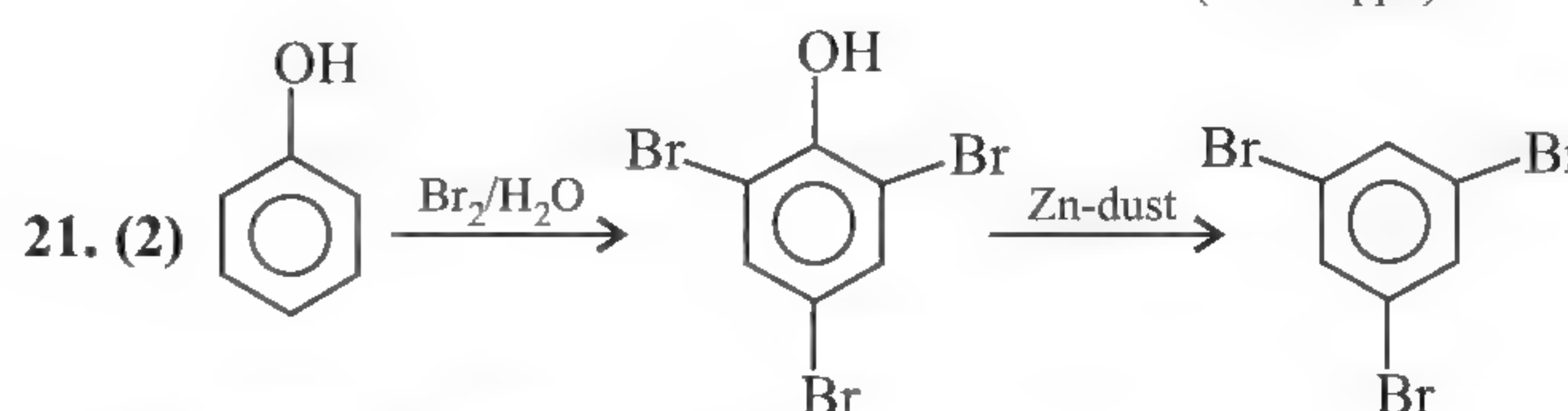
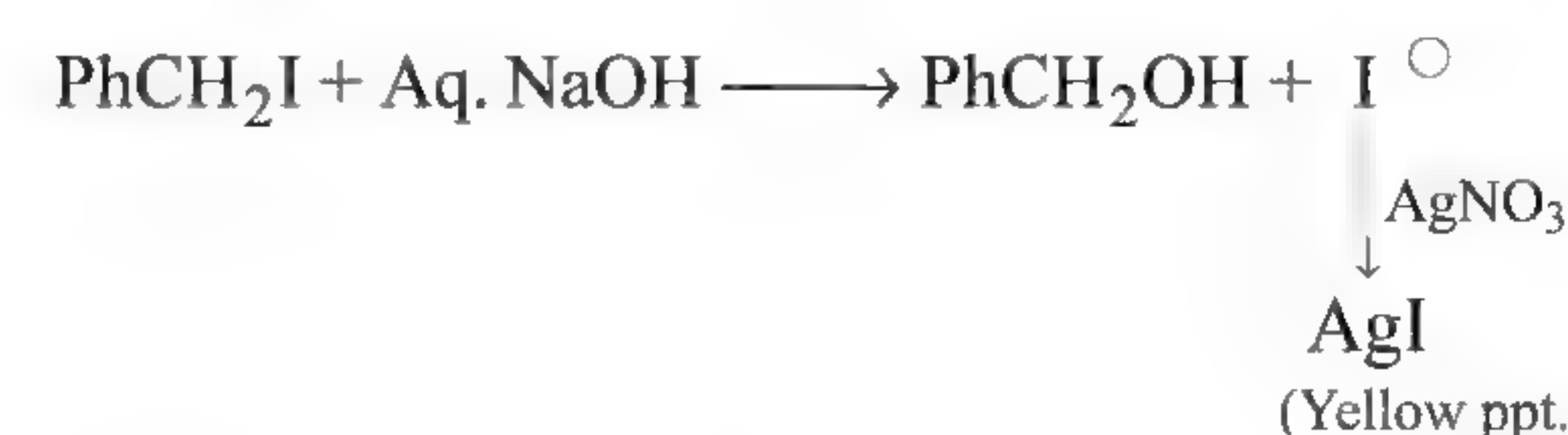
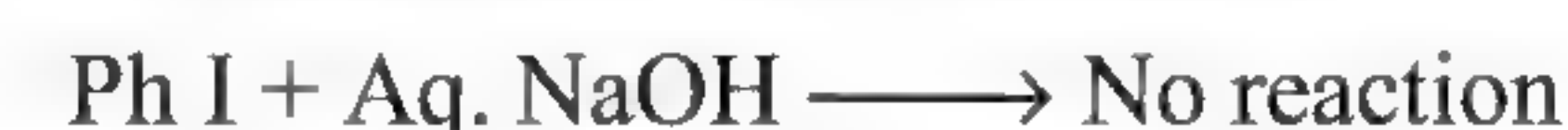


17. (3)

18. (1) See Section 3.20.

19. (2) The statement is self-explanatory.

20. (2) Aryl halide due to resonance does not give test for halide ion, whereas benzyl halides give due to the formation of benzyl C^\oplus , which gives benzyl alcohol and I^- .

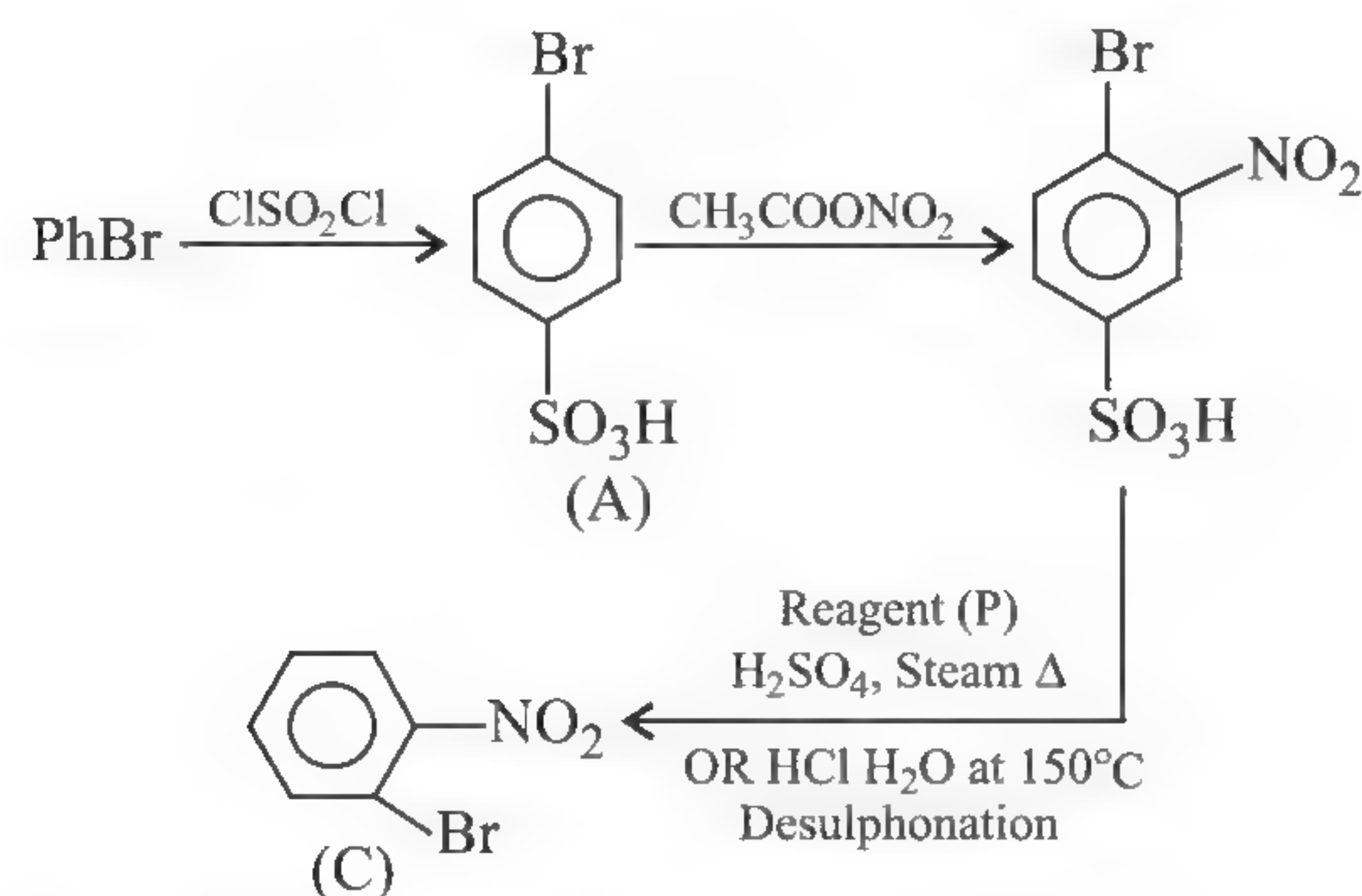


22. (2) Refer to section 3.16 (ii).

23. (2) Refer to section 3.16(b).

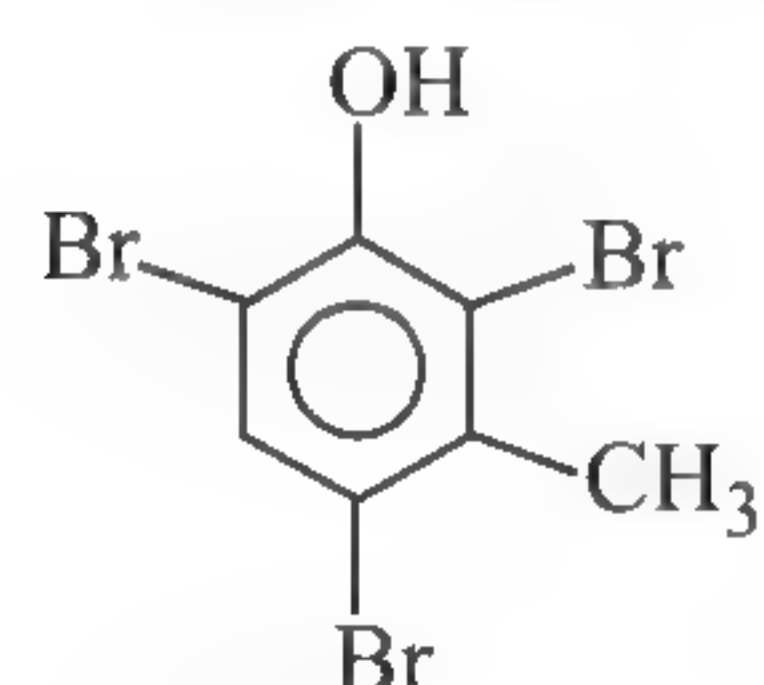
Benzoylation of alcoholic, phenolic, aliphatic or aromatic amines is called Schotten-Baumann reaction.

24. (4)



25. (4) Refer to section 3.15.

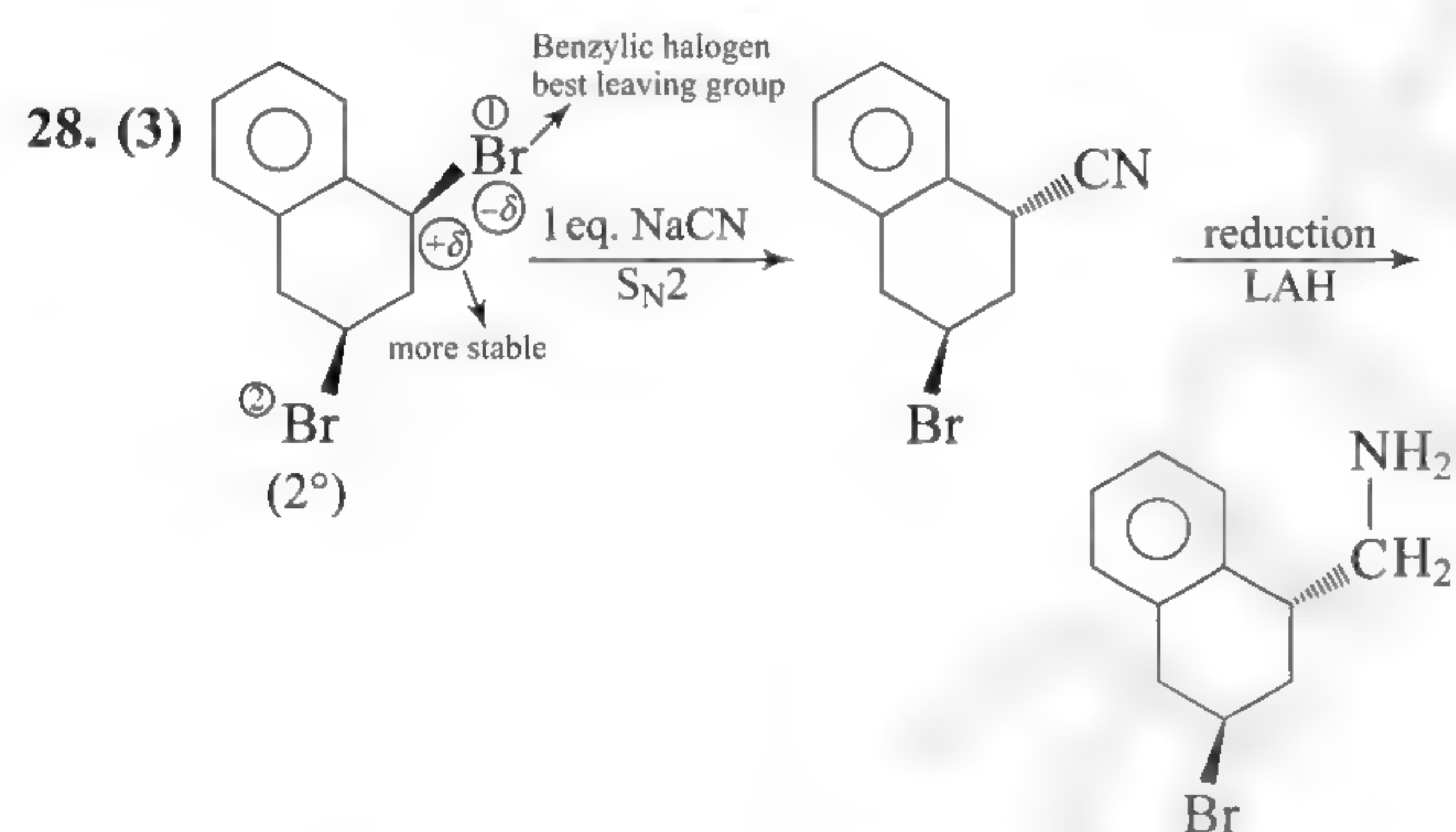
(1) and (3) are example of Ipso substitution Correct (4) is:



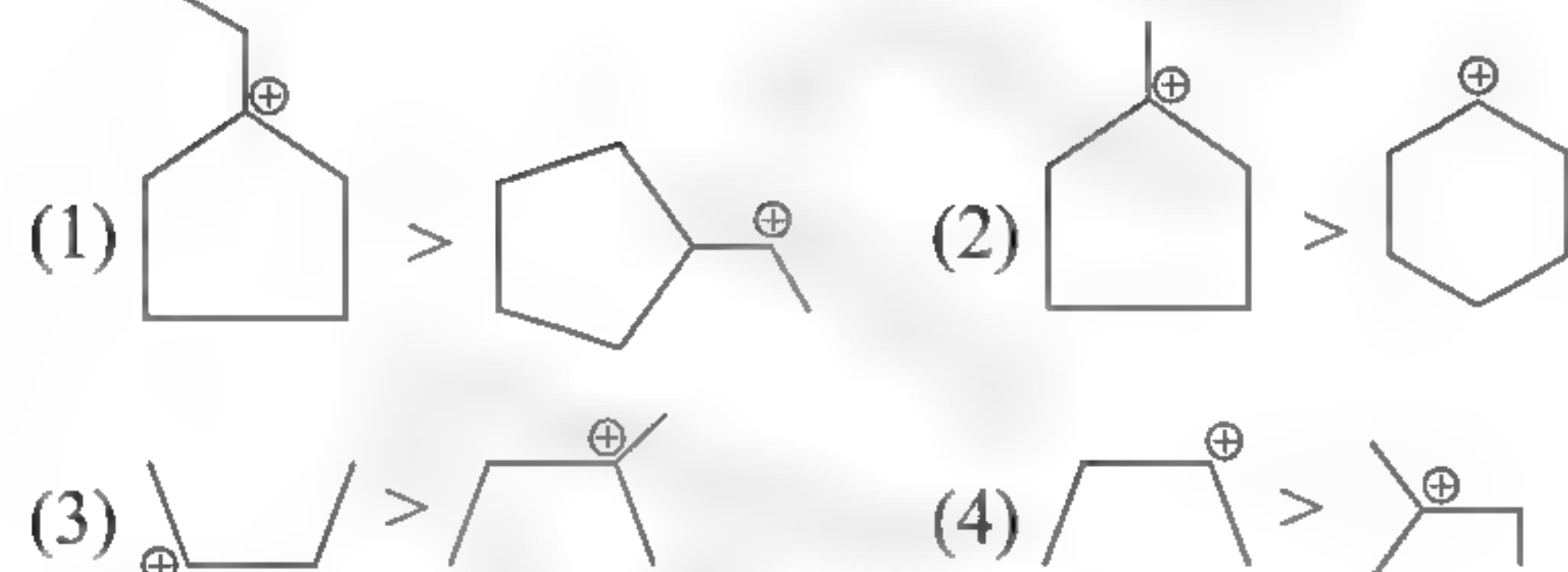
26. (4)

A \Rightarrow PhSO_3H , B \Rightarrow PhSO_3K
 C \Rightarrow PhCN , D \Rightarrow PhCOOH
 E \Rightarrow Benzene

27. (3)

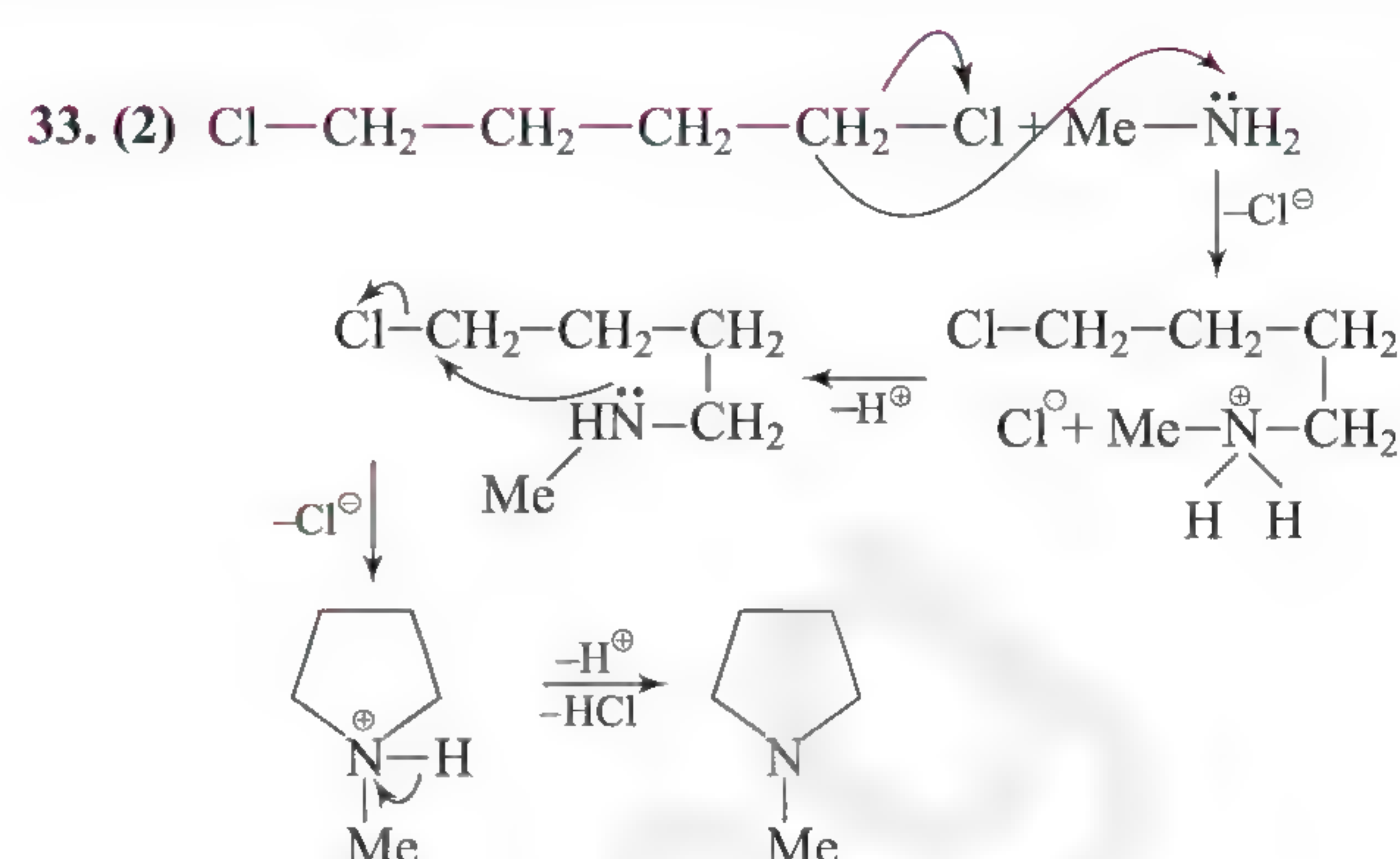
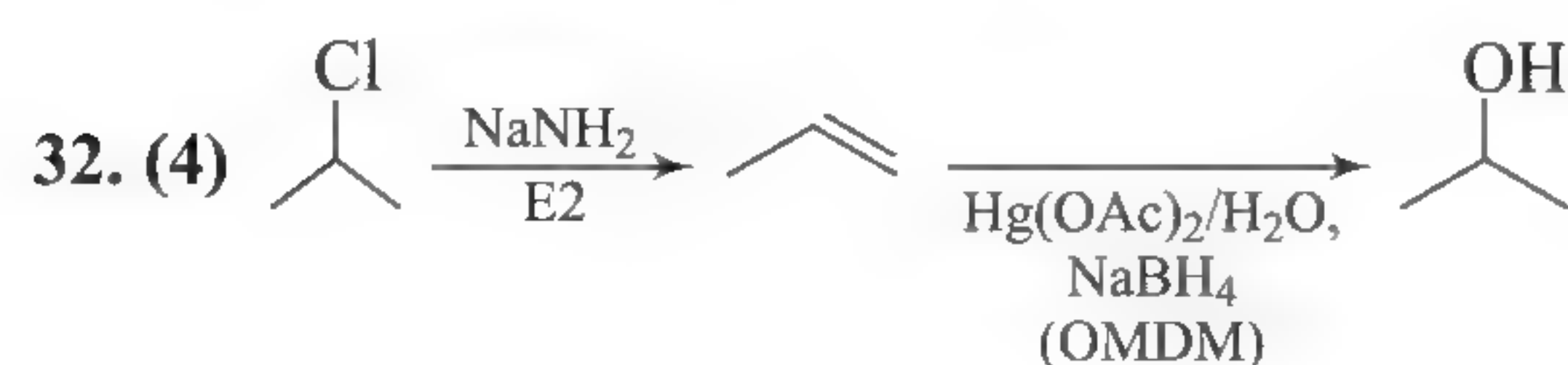


29. (4)

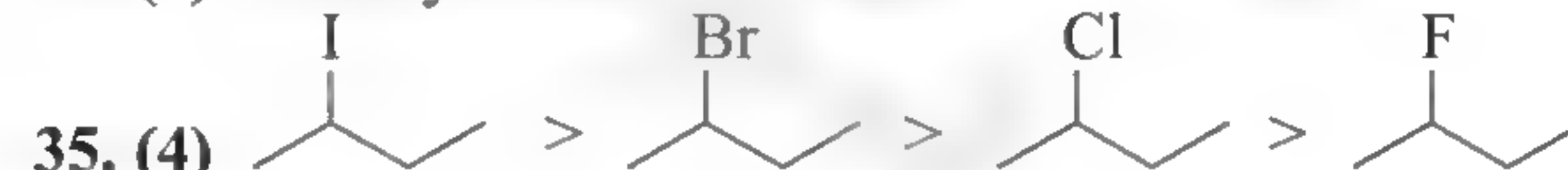


30. (1) SN^1 reaction

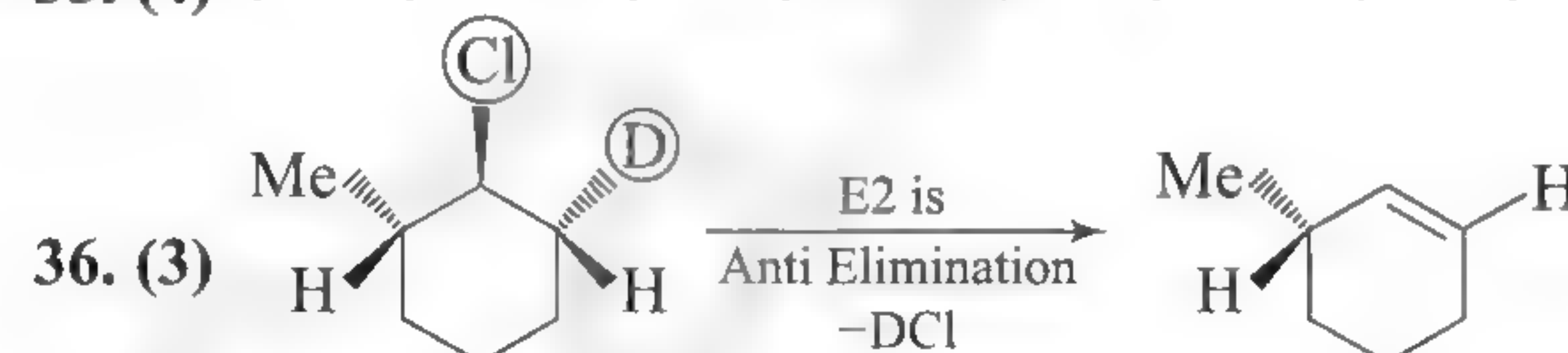
31. (3) Hydrolysis of $-\text{CN}$ substitution of $-\text{Br}$ group takes place in given reaction.



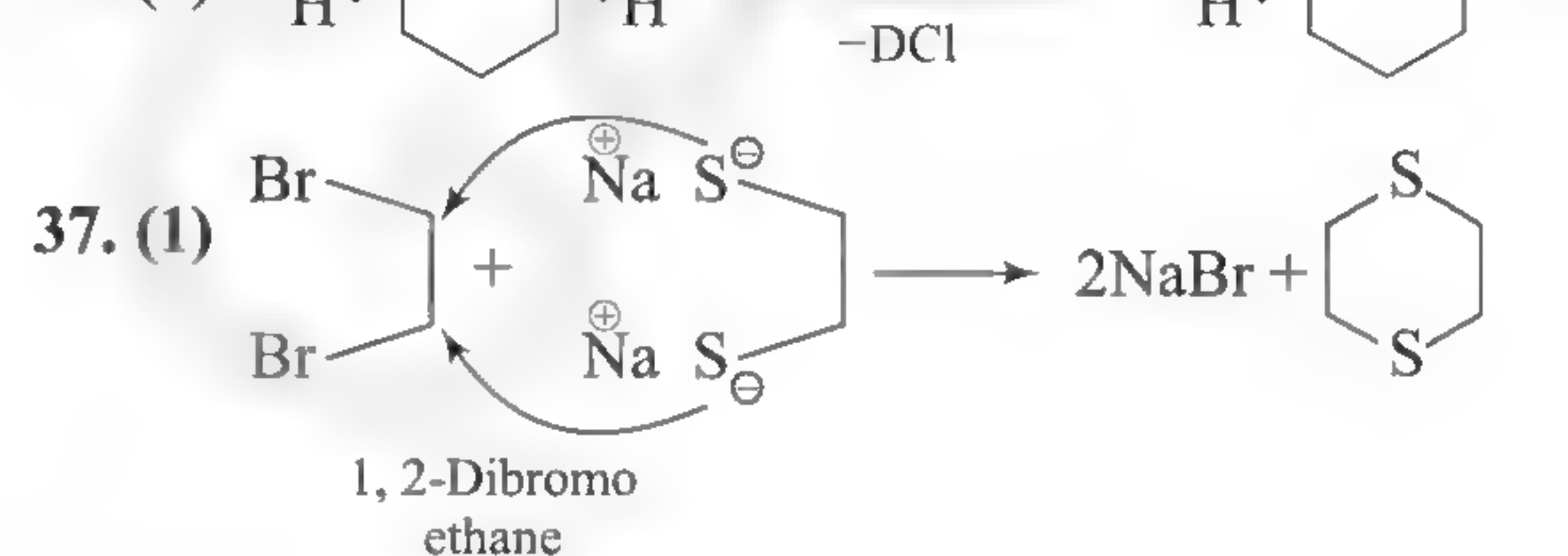
34. (1) Density \propto molecular mass



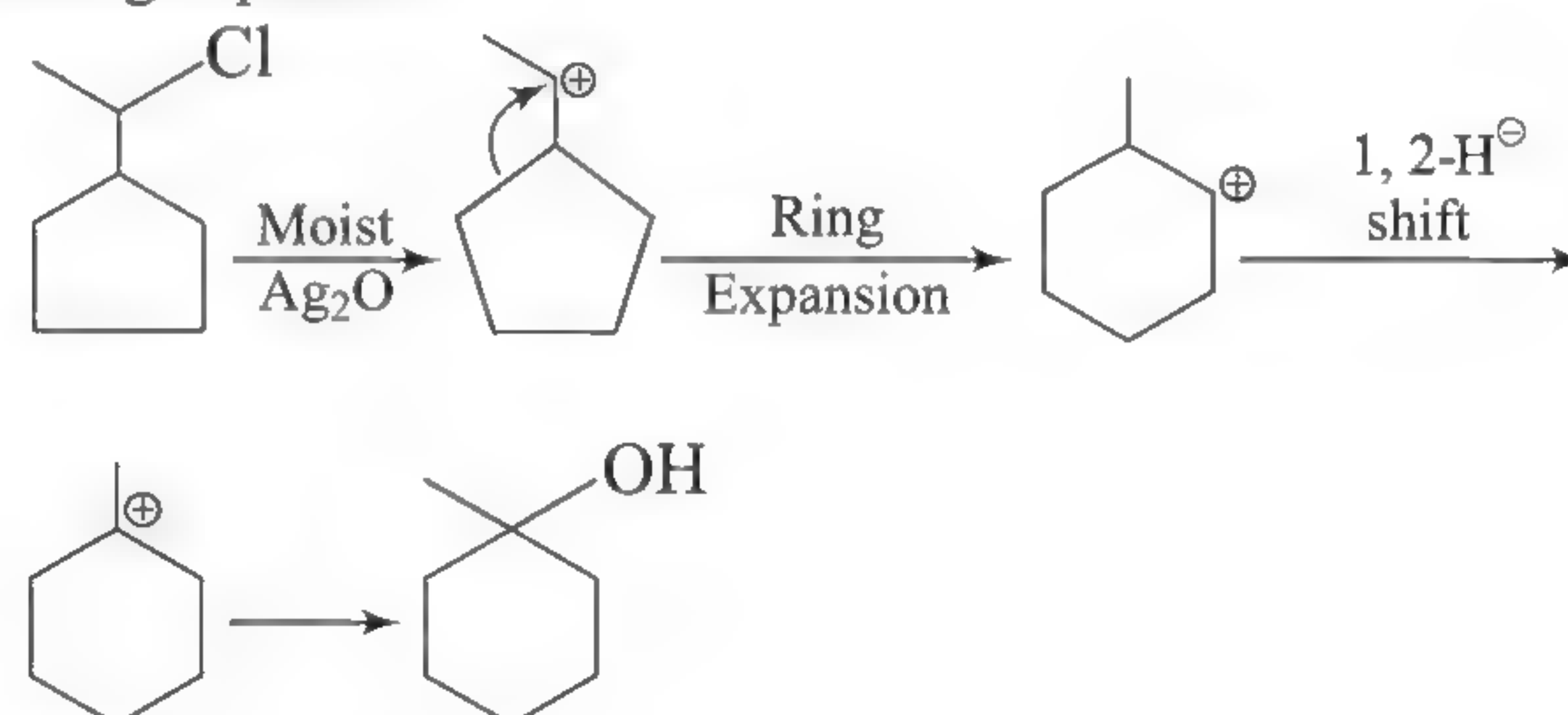
35. (4)



36. (3)



38. (3) Ring expansion

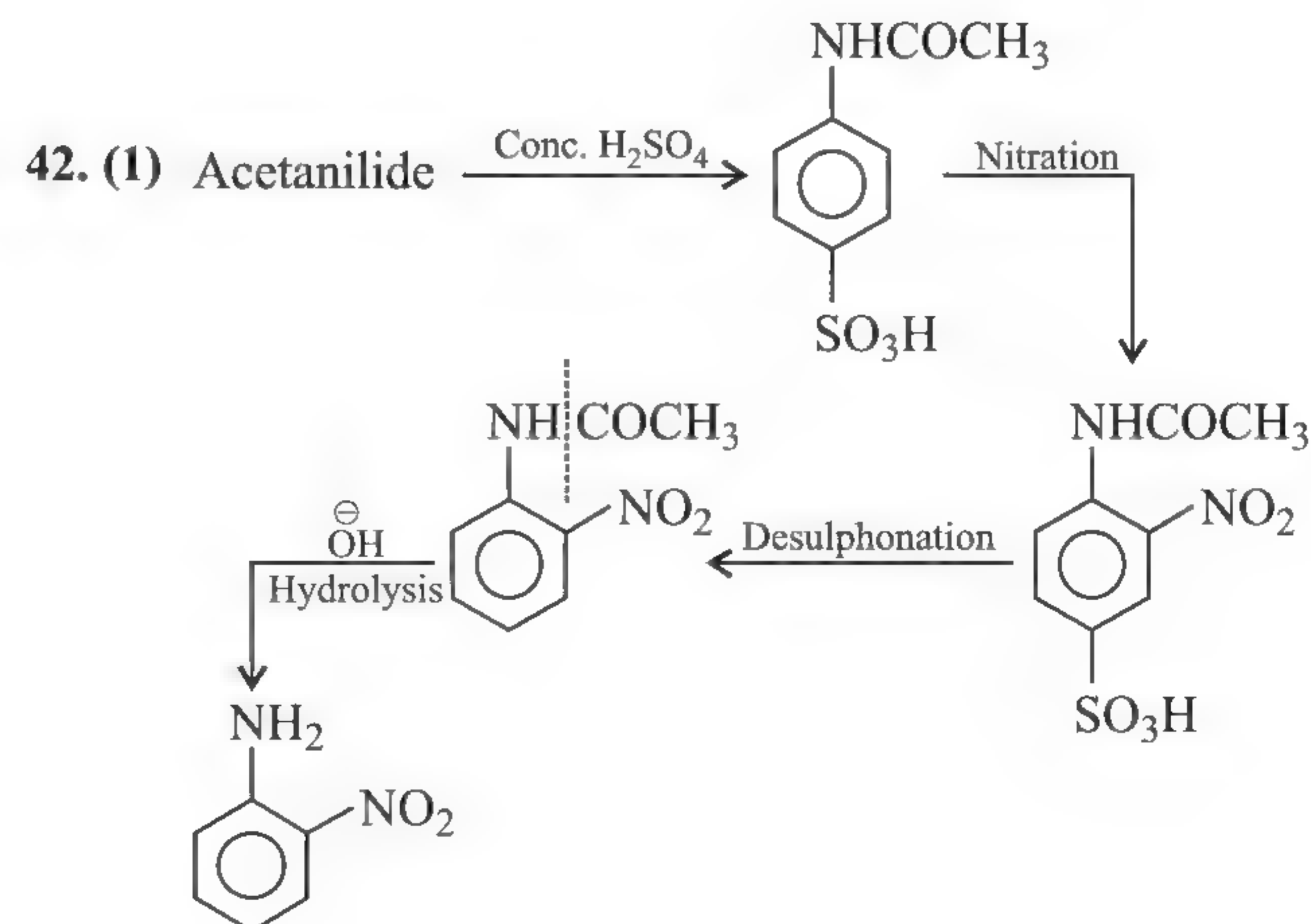
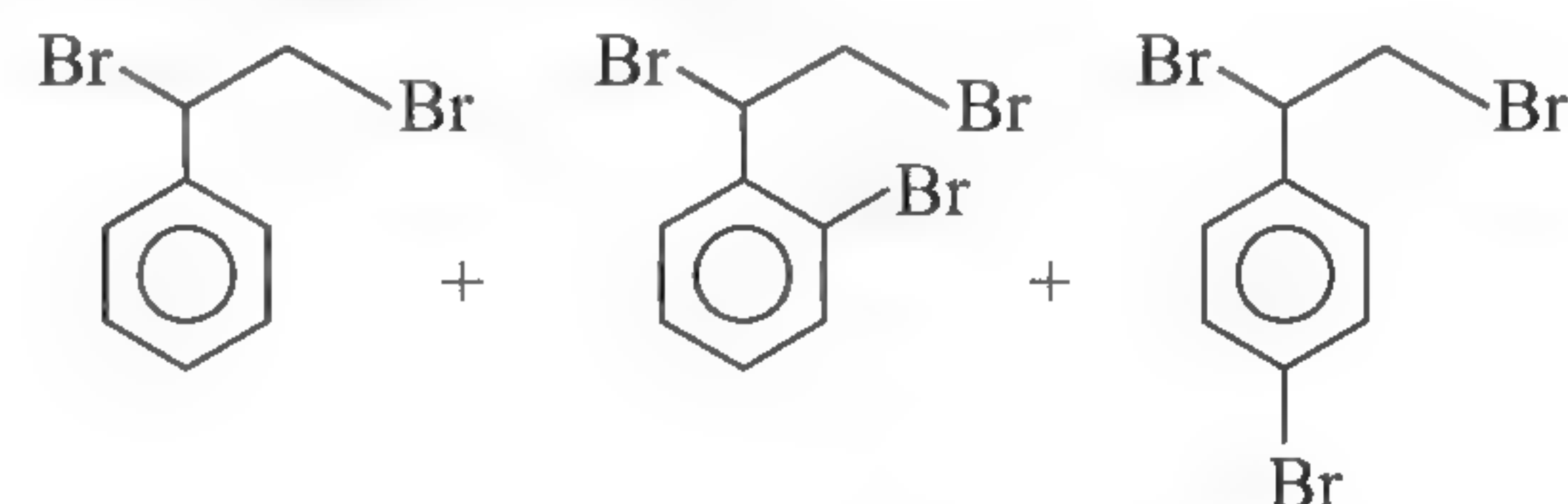


39. (4) SN^2 reaction

40. (4) Rate of $\text{SN}^2 \propto$ L. G. tendency

$$\propto \frac{1}{\text{Partial D.B. characters in C—X bond}}$$

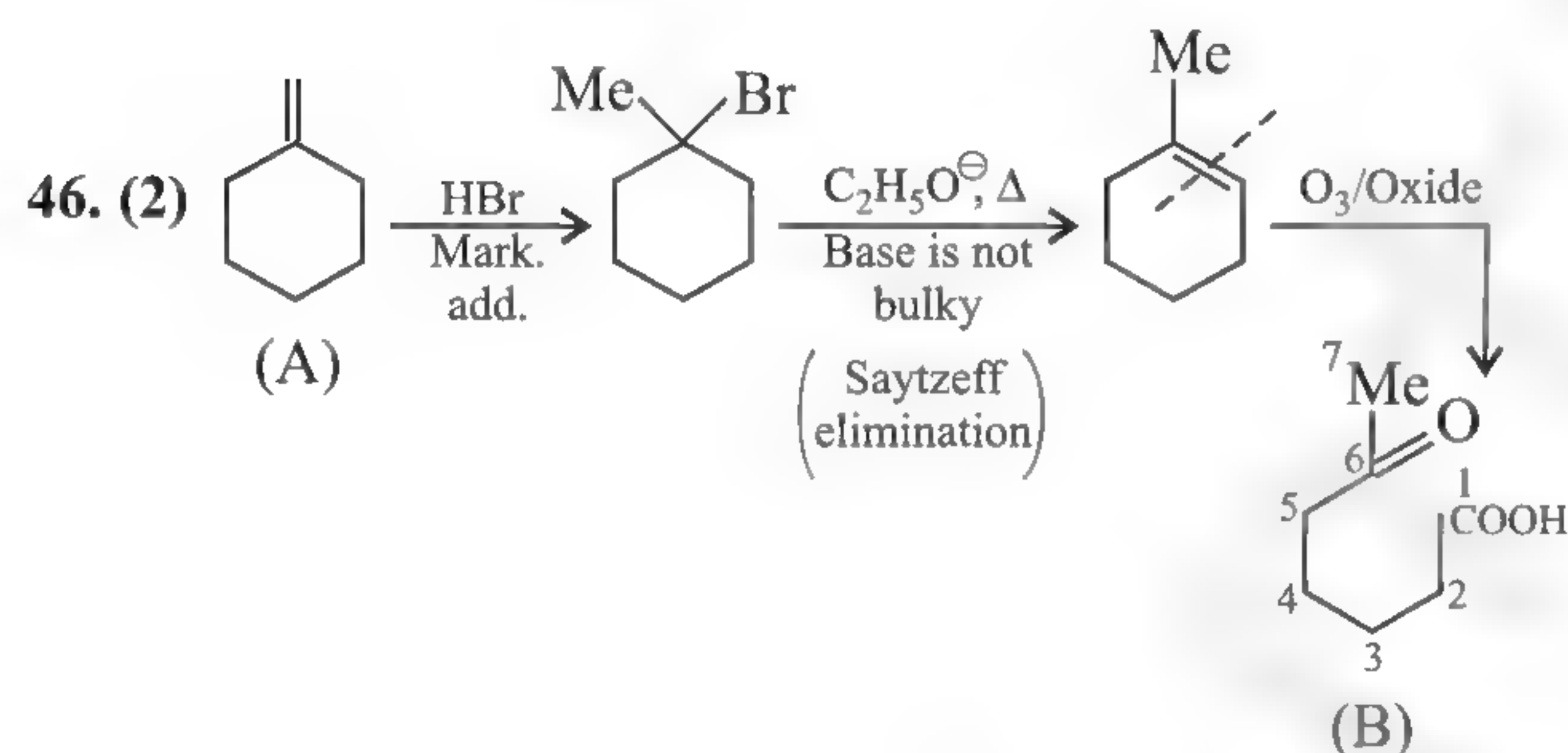
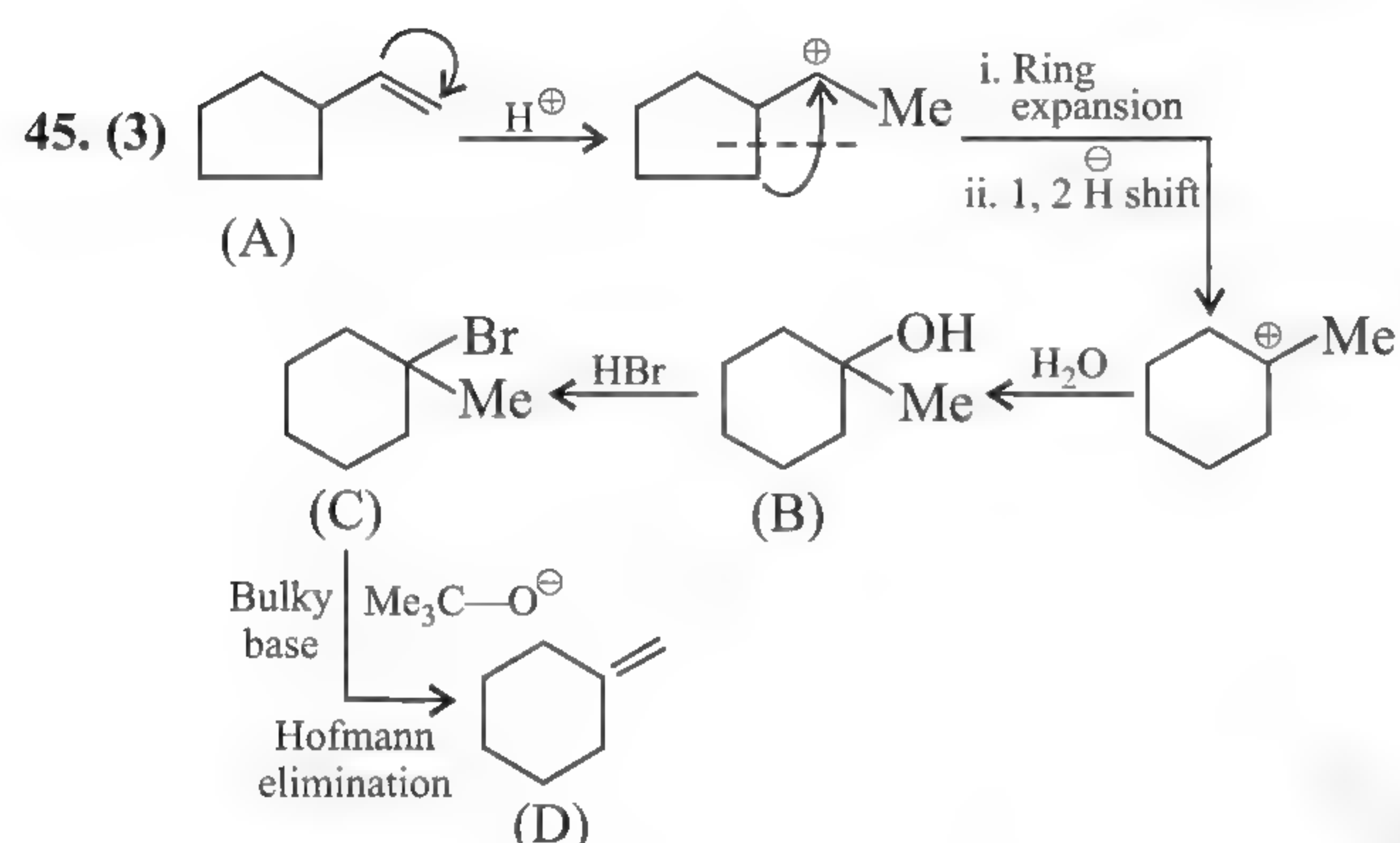
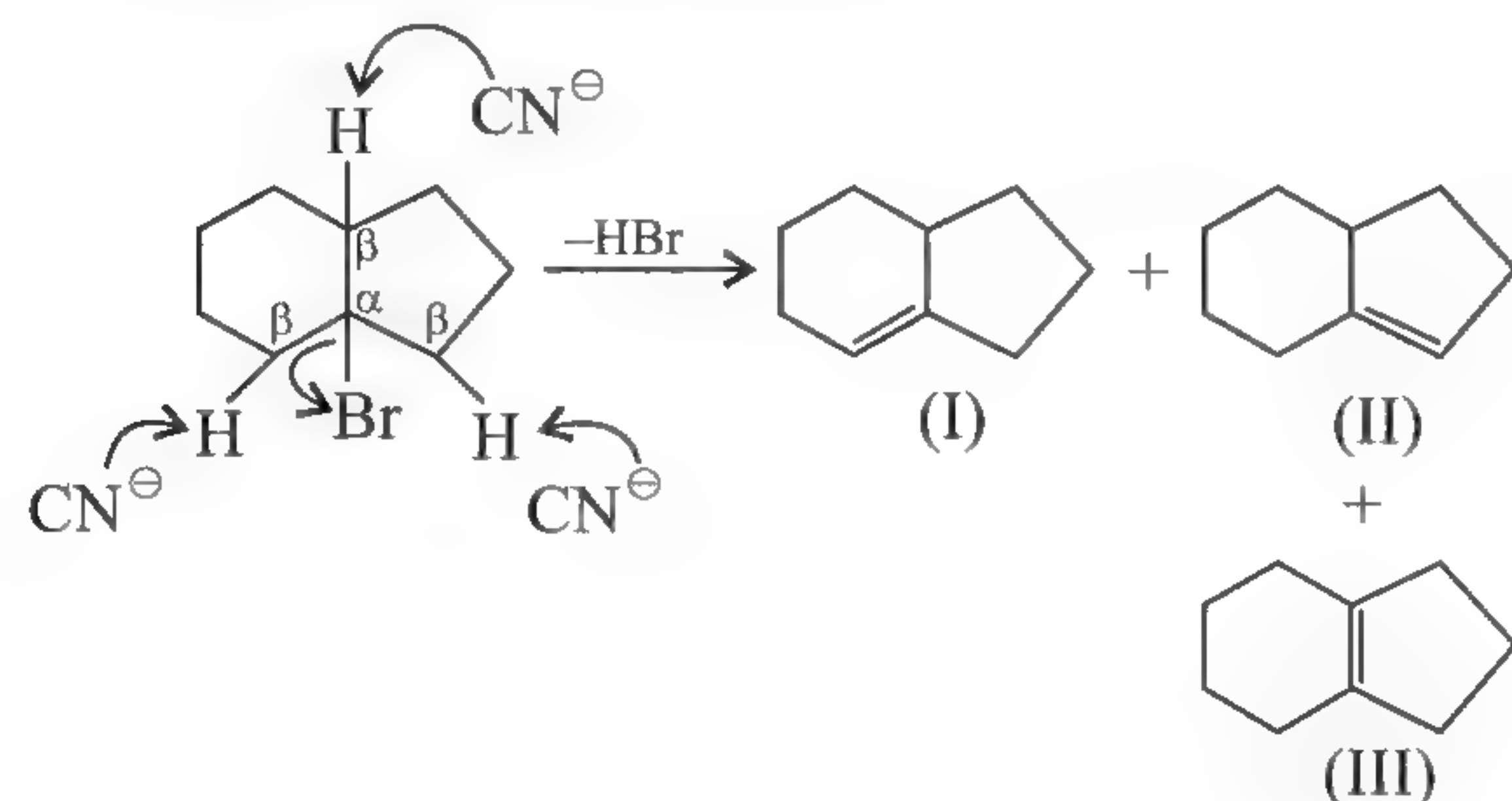
41. (3) Step 3 is wrong. The last step will first brominate the double bond. The product will be:



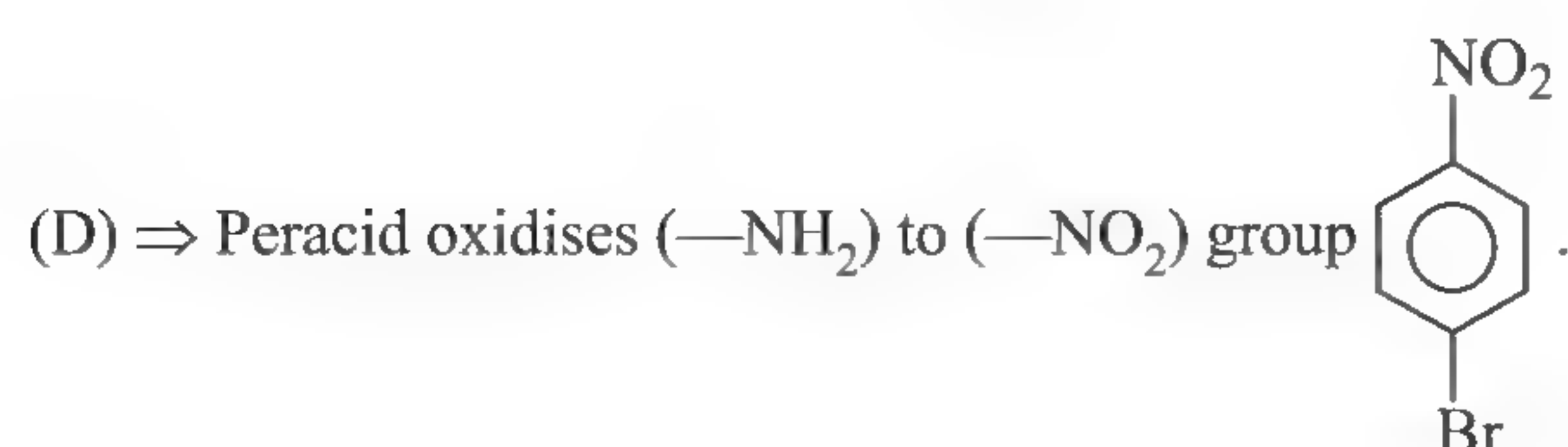
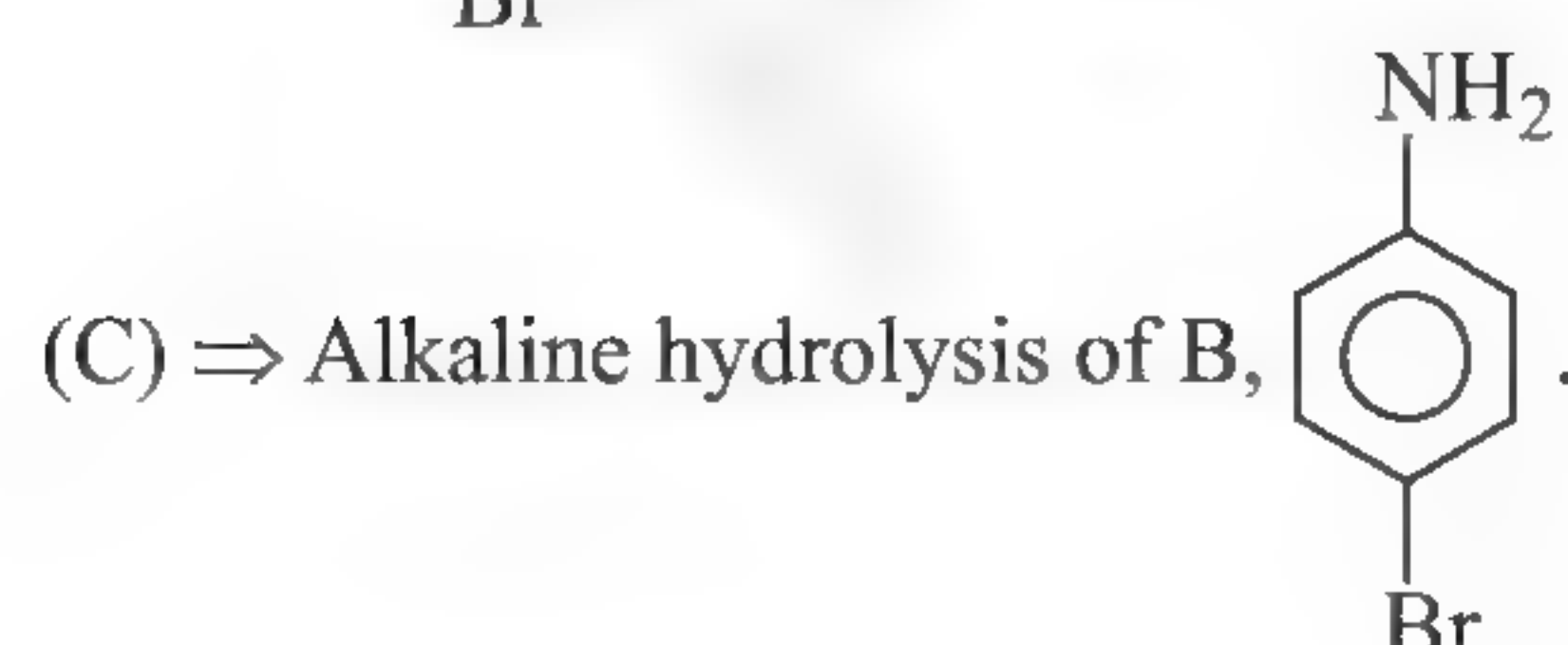
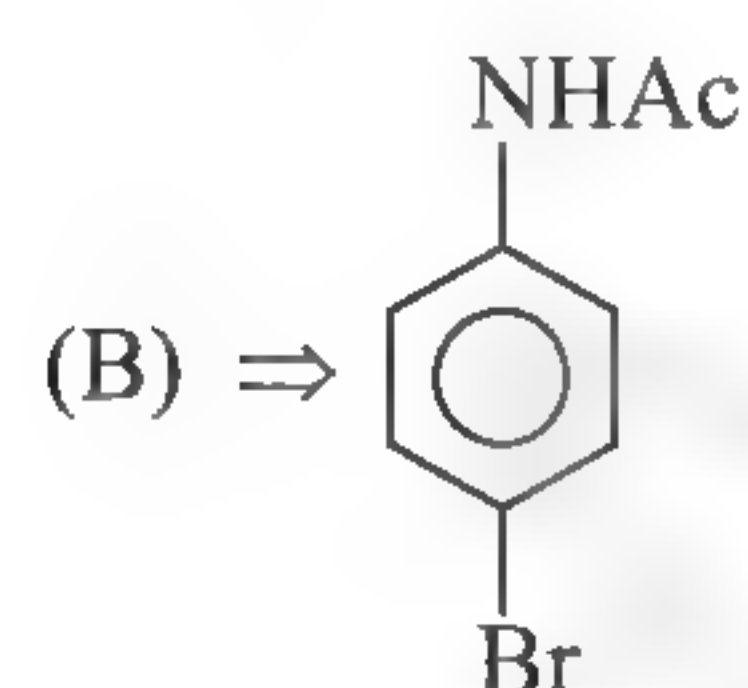
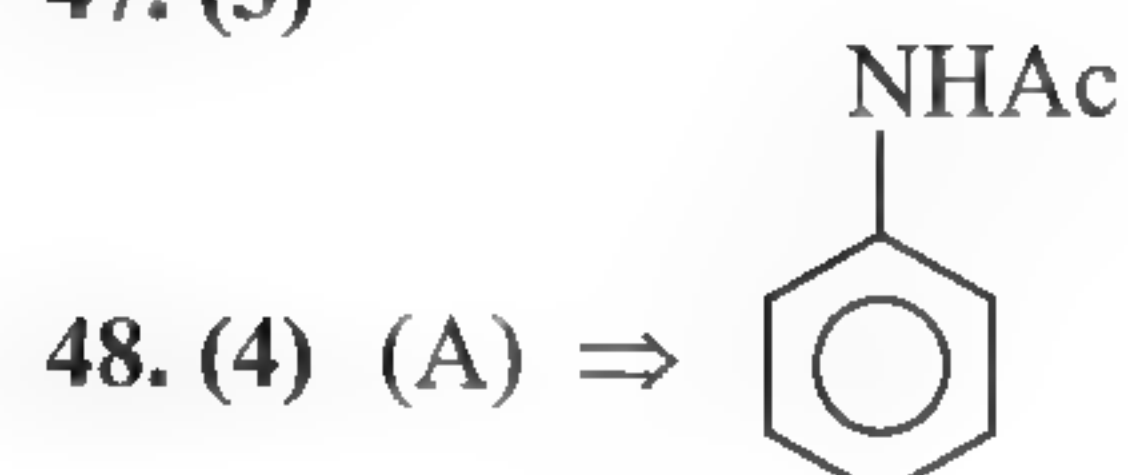
43. (3) (I) \Rightarrow 1° allylic halide and less steric hindrance, hence S_N^2 .
 (III) \Rightarrow 3° allylic halide, most stable carbonium ion and hence S_N^1 .

44. (1) Since the reactant is a 3° alkyl halide, so in the presence of NaCN , it will follow $\text{E}2$ path rather than S_N^2 , so path (II) is not feasible.

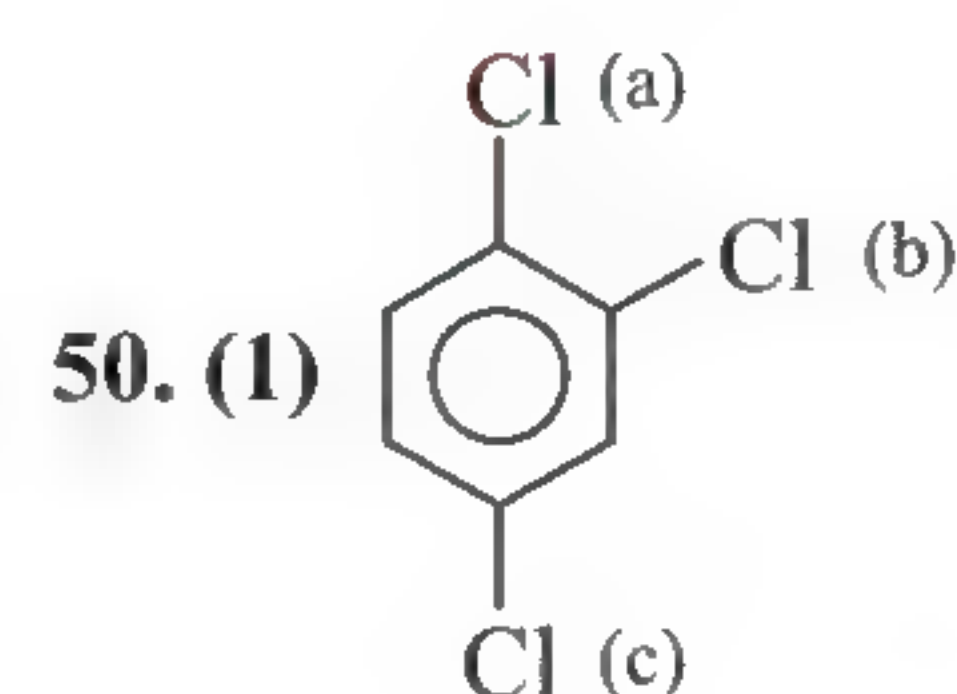
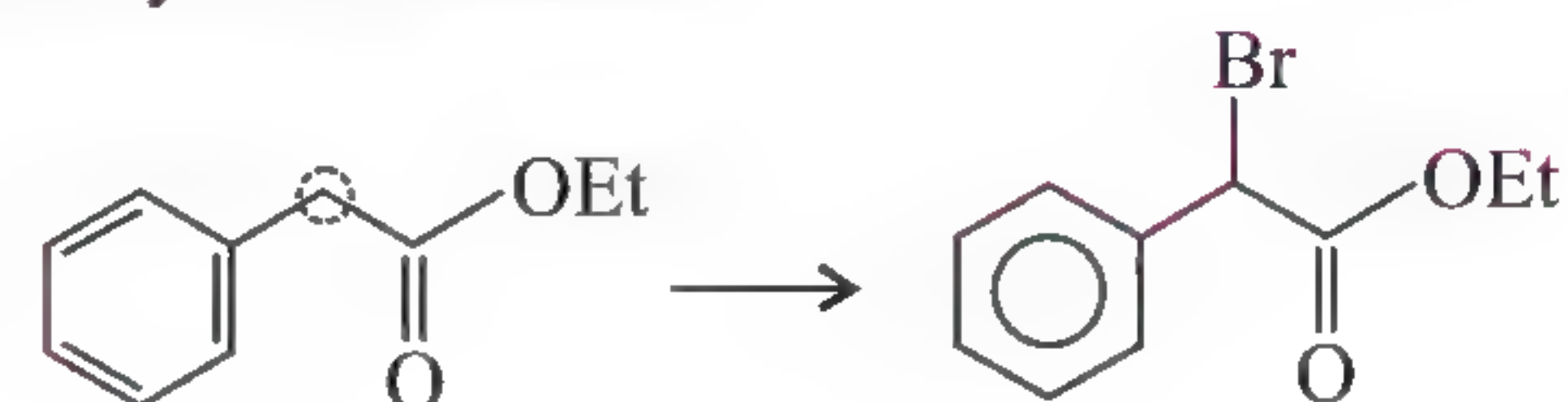
The possible product by path (II) is:



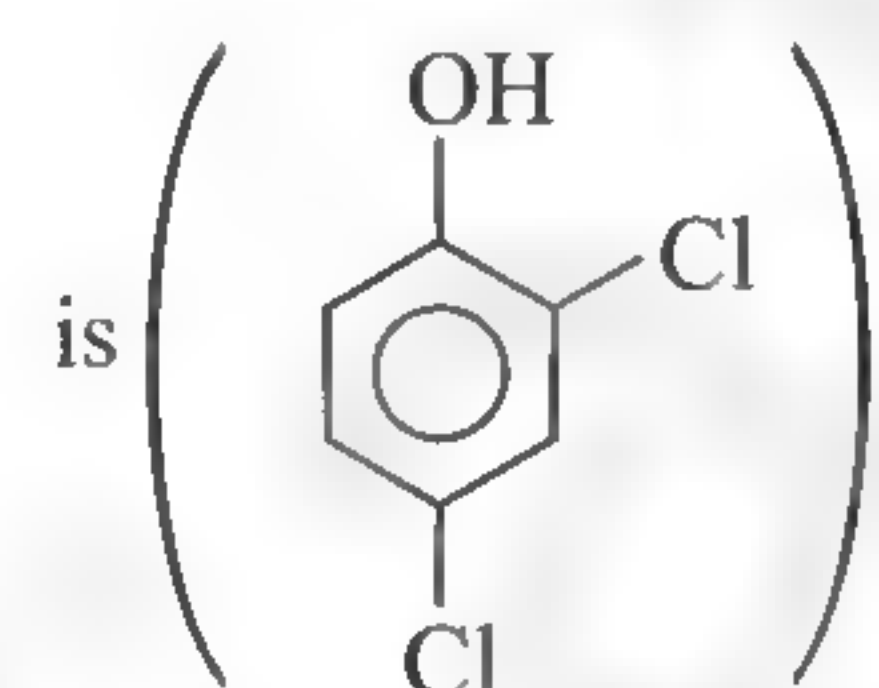
47. (3)



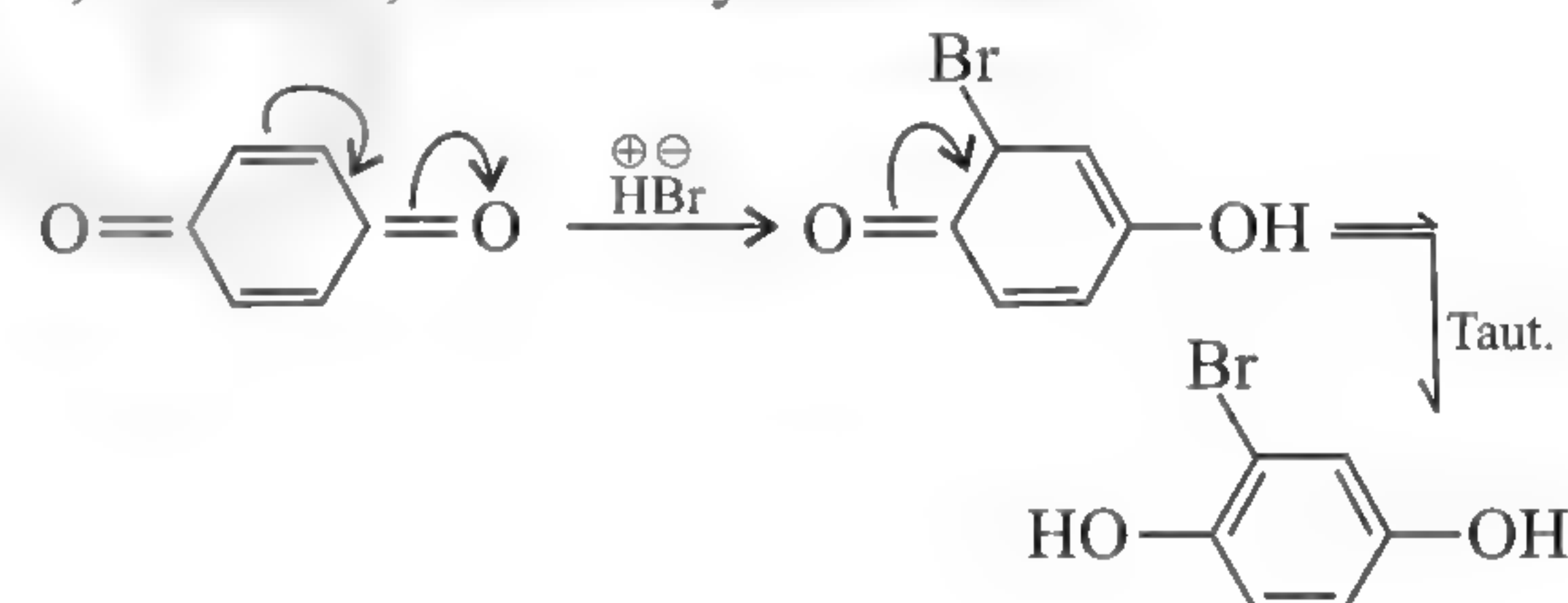
49. (2) Allylic bromination



Cl (a) is more reactive towards ArS_N reaction because two EWGs are at o - and p -positions w.r.t. Cl (a). Hence, the product



51. (3) 1,4-Addition, followed by tautomerism.



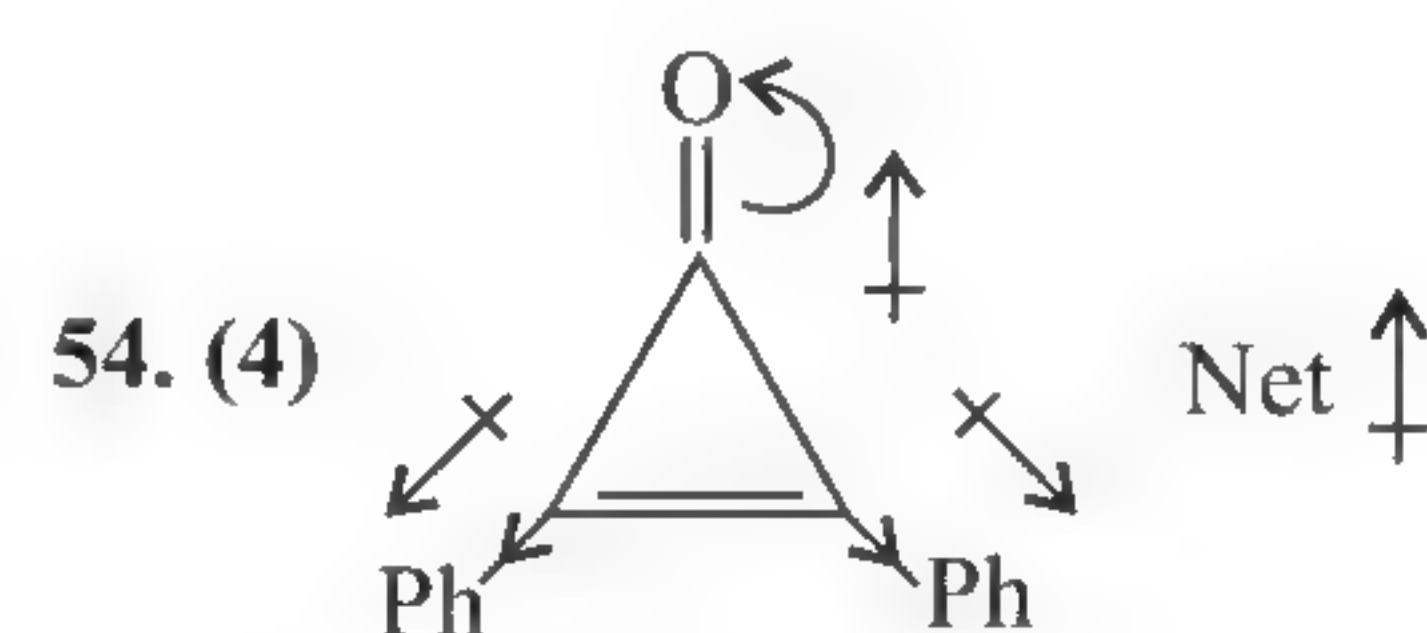
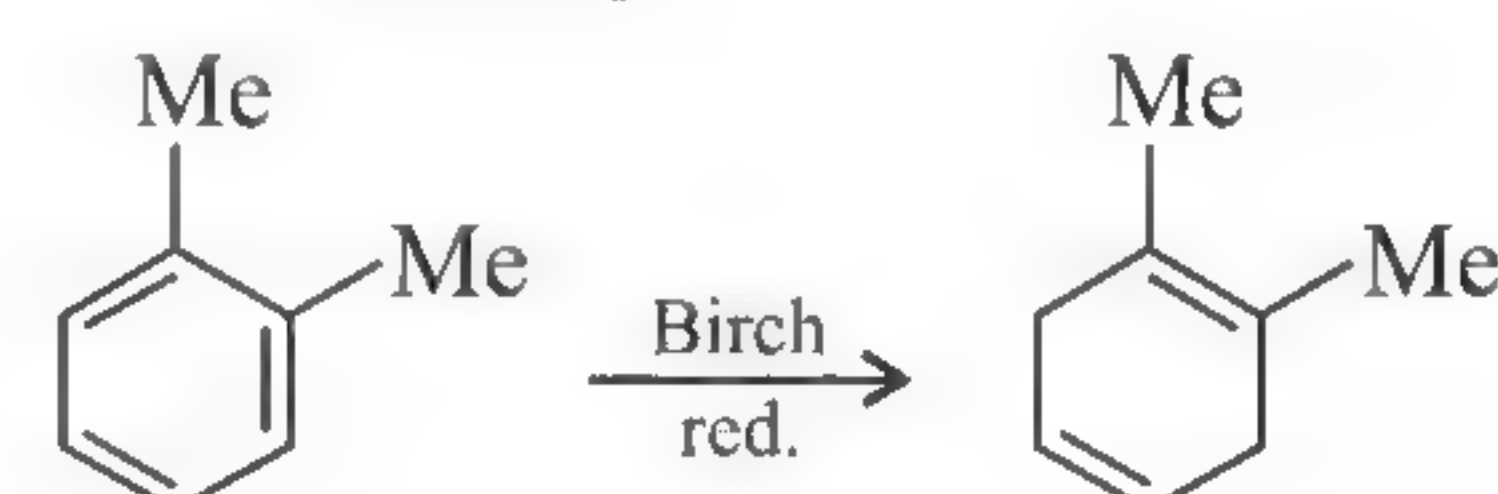
52. (3) More the EWG, more is the reactivity for ArS_N reaction.

$-\text{SO}_3\text{H}$ (more resonance structure)

$> -\text{NO}_2 > \text{Cl} > \text{Me}$ (EDG)

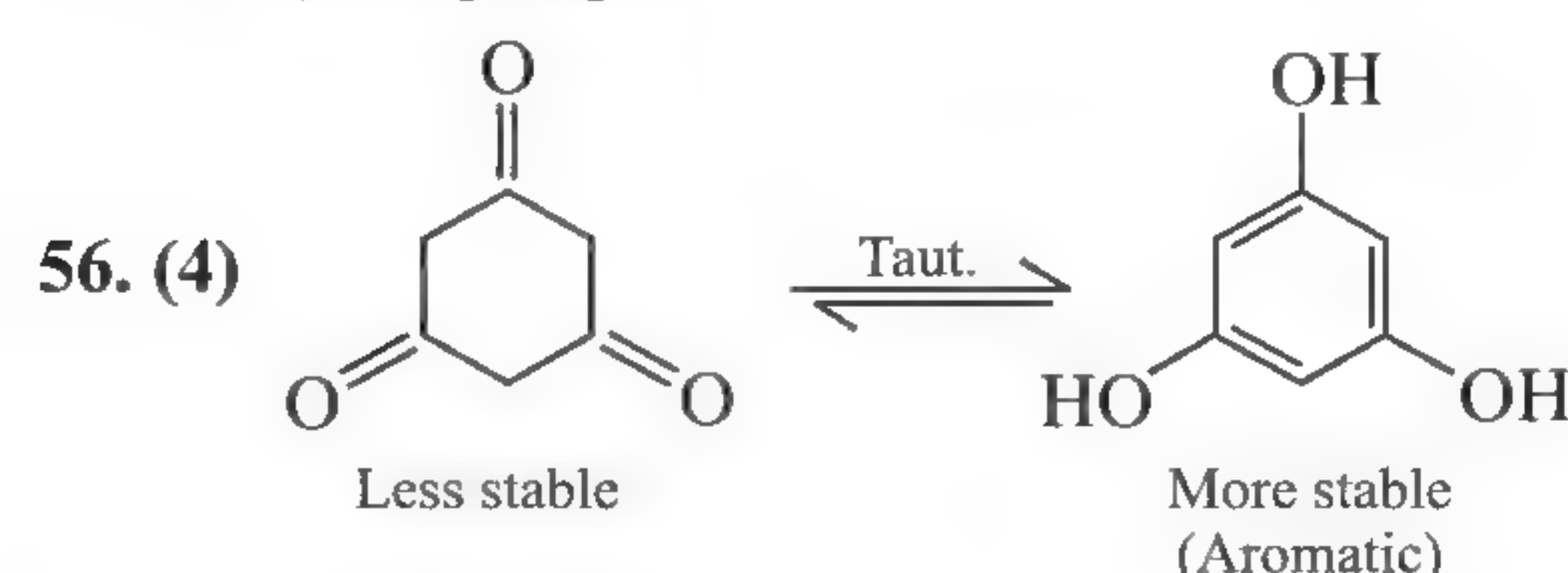
Therefore, (III) $>$ (IV) $>$ (II) $>$ (I).

53. (1) It is Birch reduction to give isolated double bond attached to the (Me) group.



Net dipole vector is more in (4).

55. (2) In (2), positive charge is more stabilised due to $+I$ effect of (Me) group.



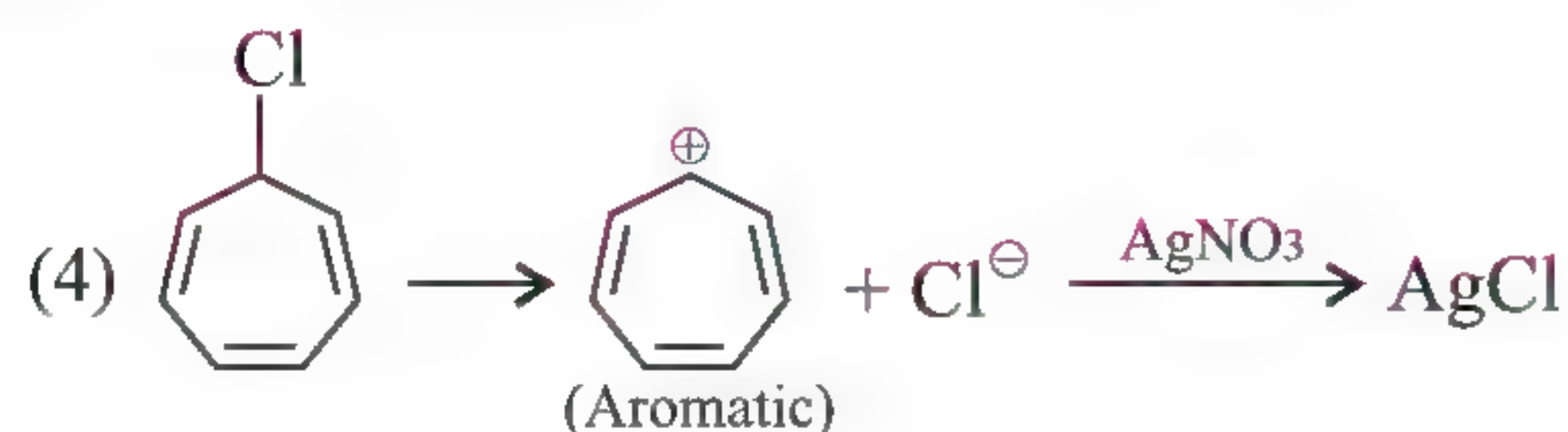
57. (4)

(1) It is aryl halide, stabilised by resonance.

(2) Vinyl chloride is also stabilised by resonance.

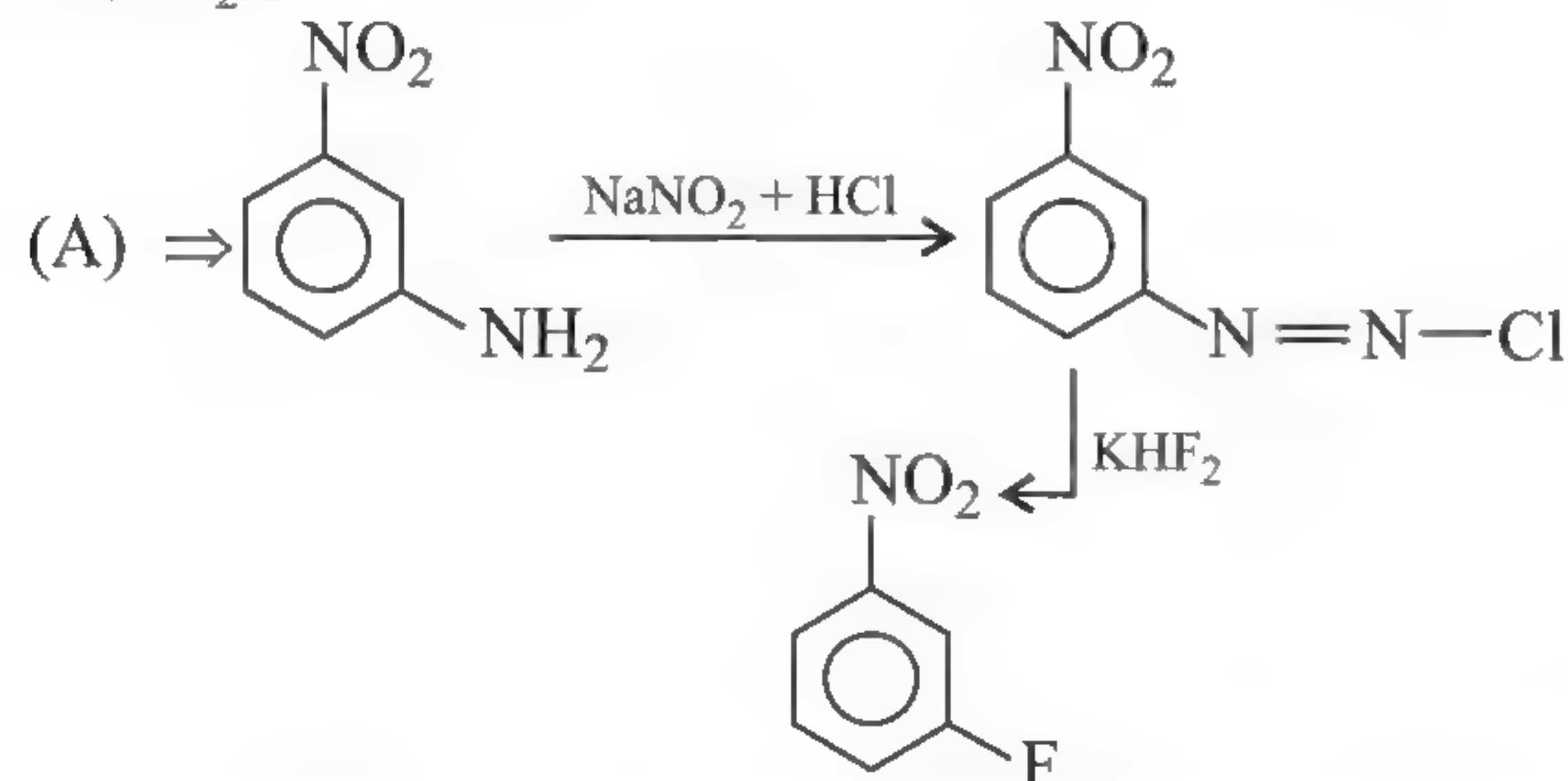


(3) Vinyl system as in (2).

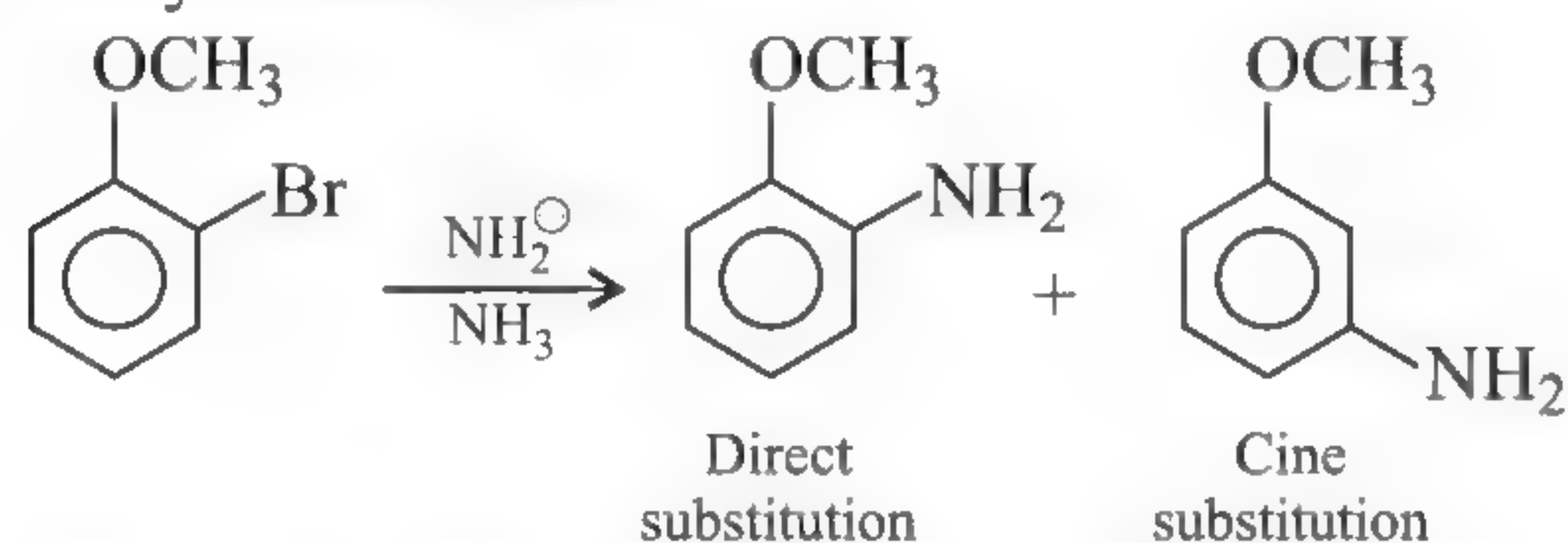


58. (1) It is more reactive towards SE reactions, due to hyperconjugation.

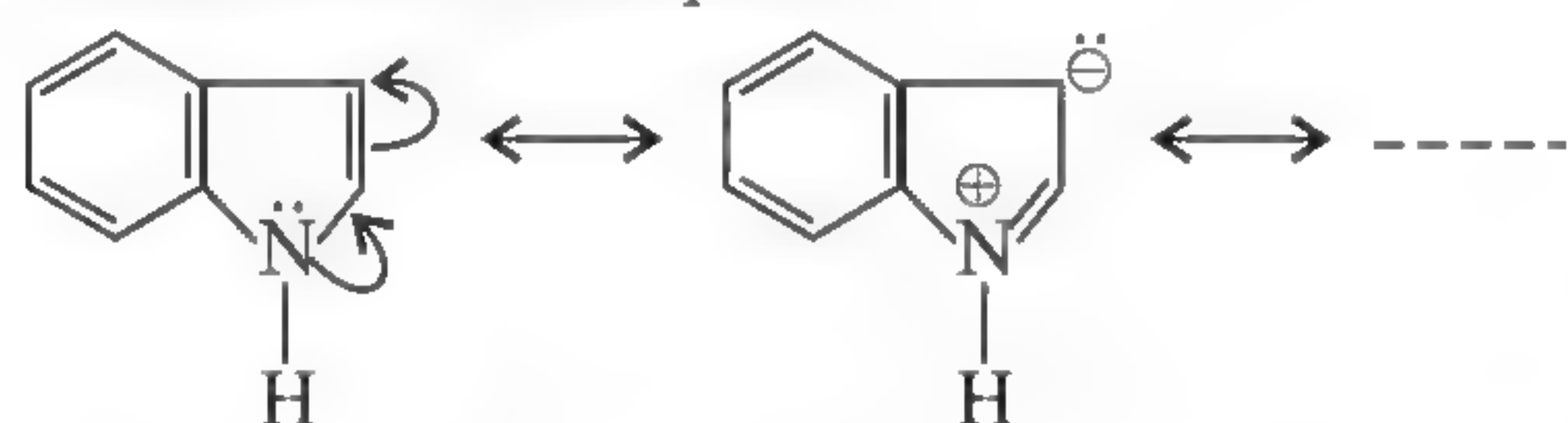
59. (2) Selective reduction by NH₄HS [only one (—NO₂) is reduced to (NH₂)].



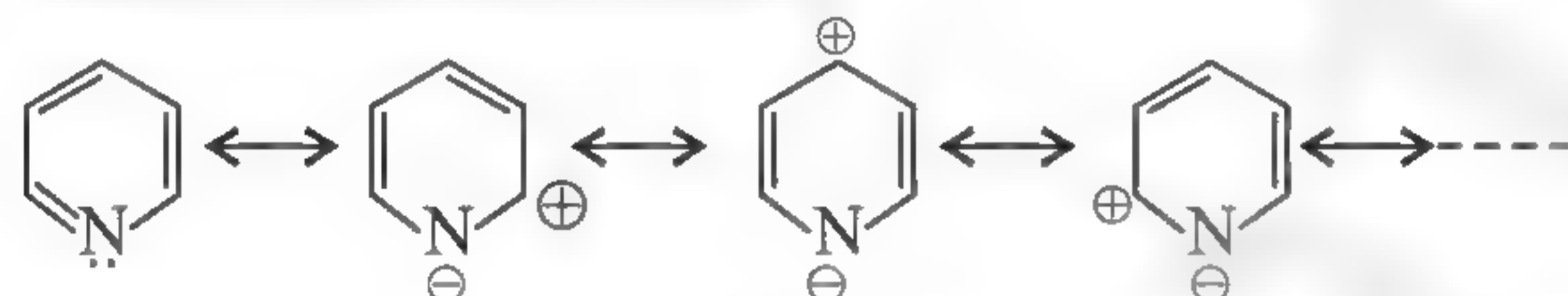
60. (1) It is an example of ArSN (elimination–addition) reaction *via* benzyne intermediate.



61. (1) Due to resonance, C-3 acquires a negative charge and SE reaction at C-3 takes place.

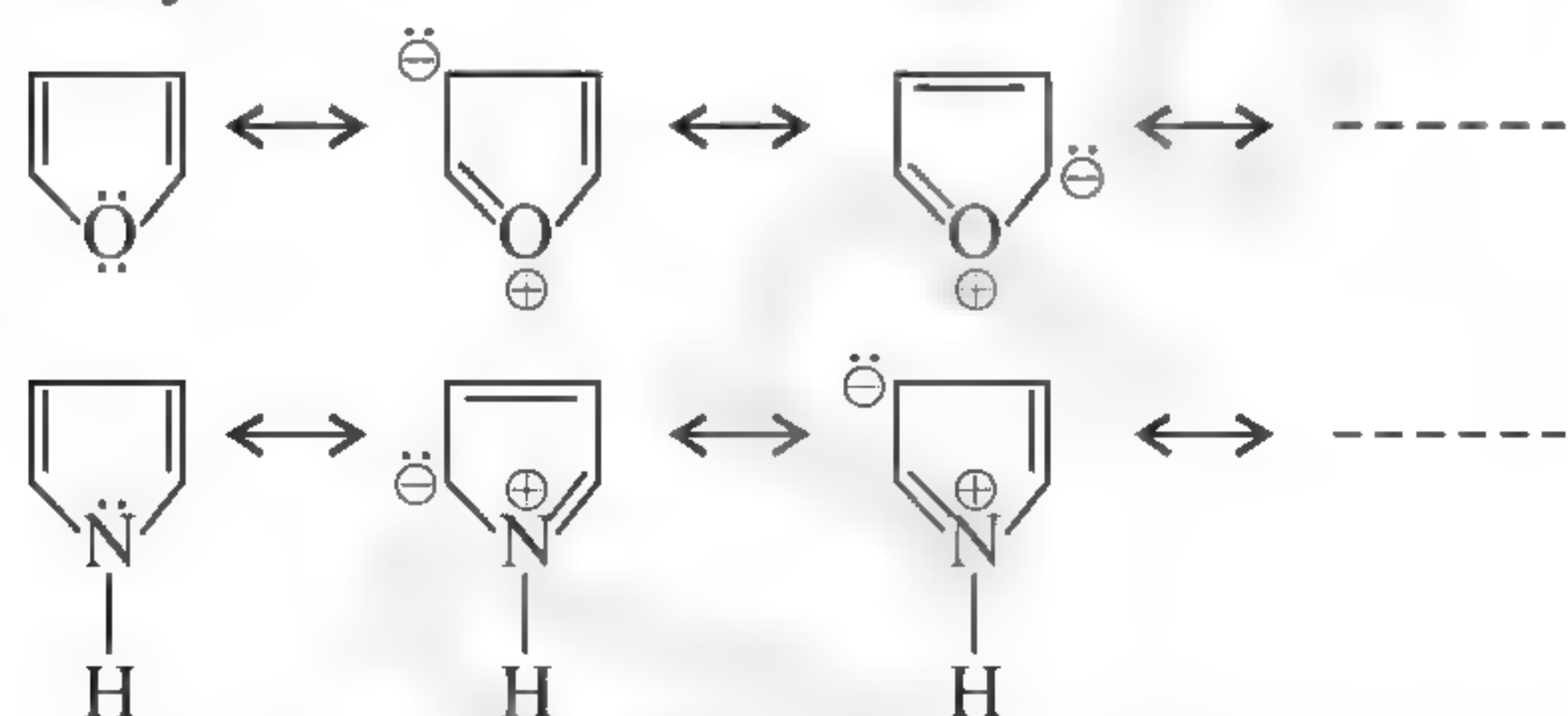


62. (1) Pyridine is least reactive towards SE because pyridine is resonance stabilised as shown.

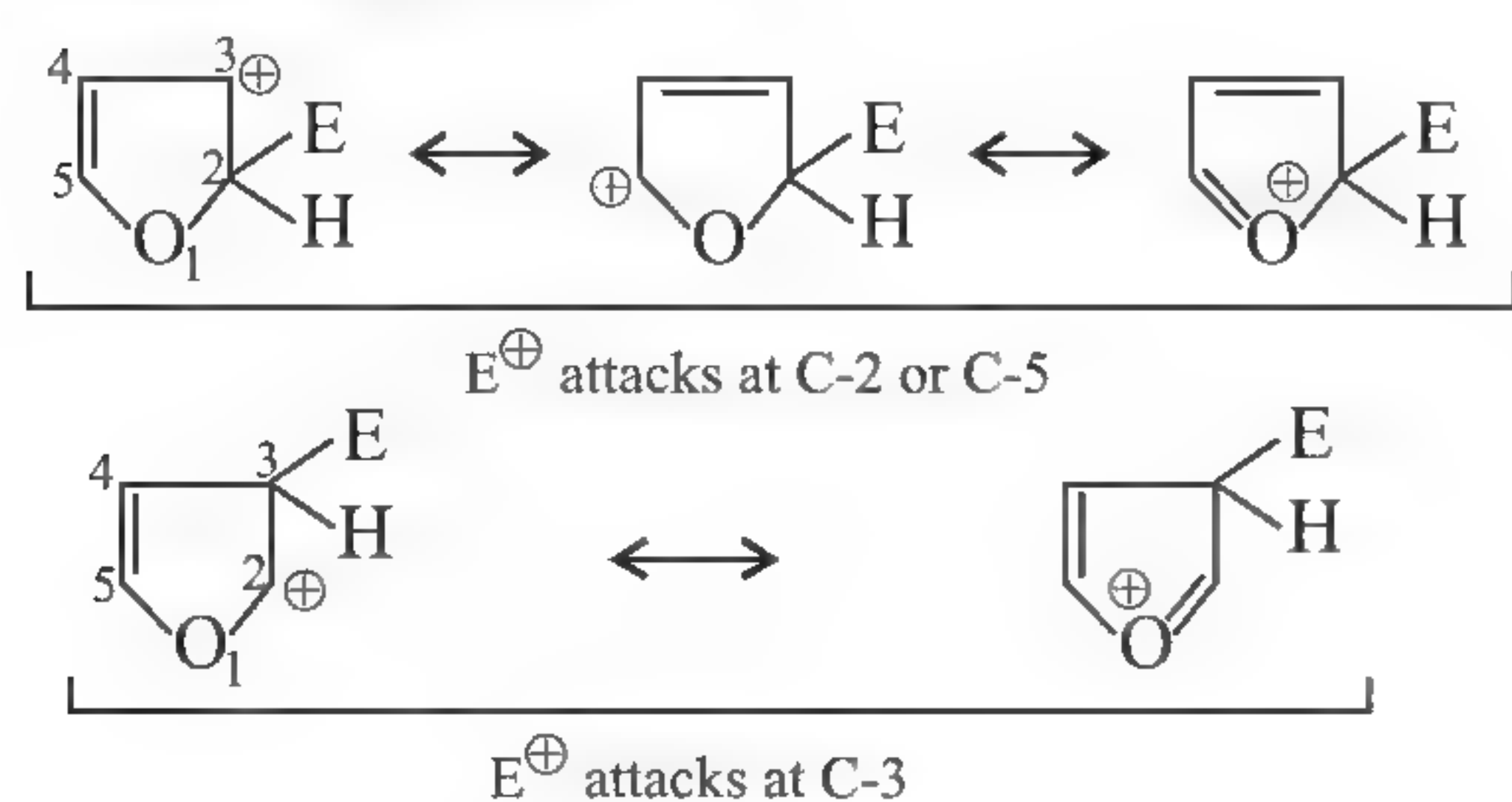


Because of withdrawal of \bar{e} 's from the ring by N atom, the ring is deactivated, thereby resembling the benzene ring in nitrobenzene. So, it is least reactive towards SE reaction.

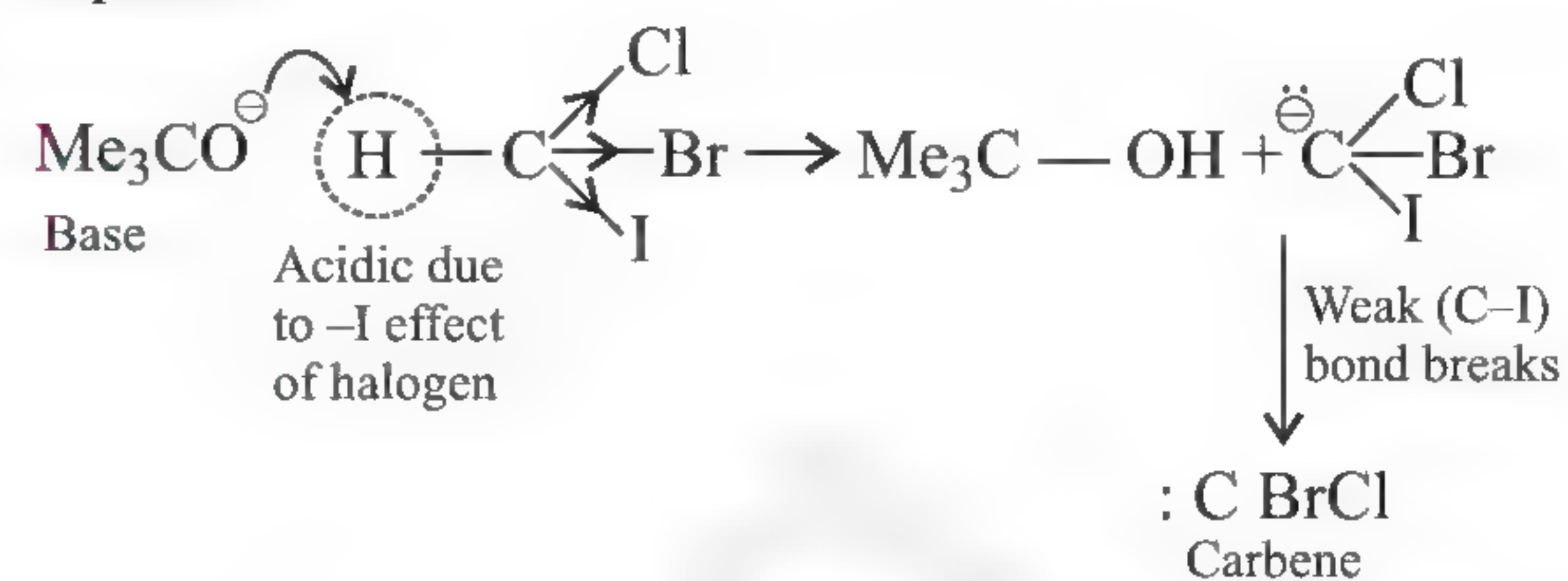
(2) and (4) are resonance structures so SE reaction takes place easily.



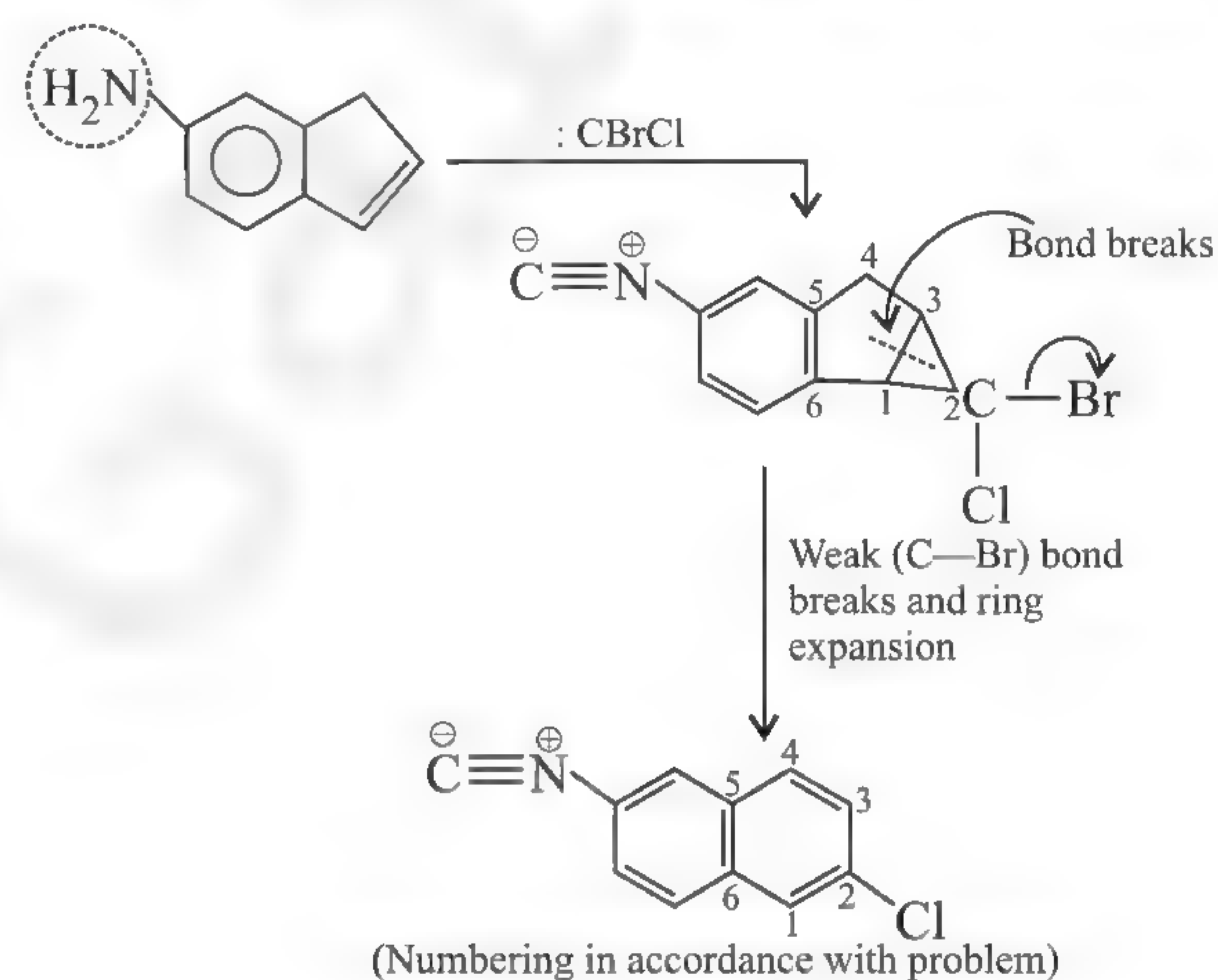
SE reaction in pyrrole, thiophene, and furan takes place at C-2 or C-5 positions because there are three resonating structures when E[⊕] attacks at C-2 or C-5 and two resonating structures when E[⊕] attacks at C-3.



63. (4) Reaction takes place by carbene mechanism followed by ring expansion

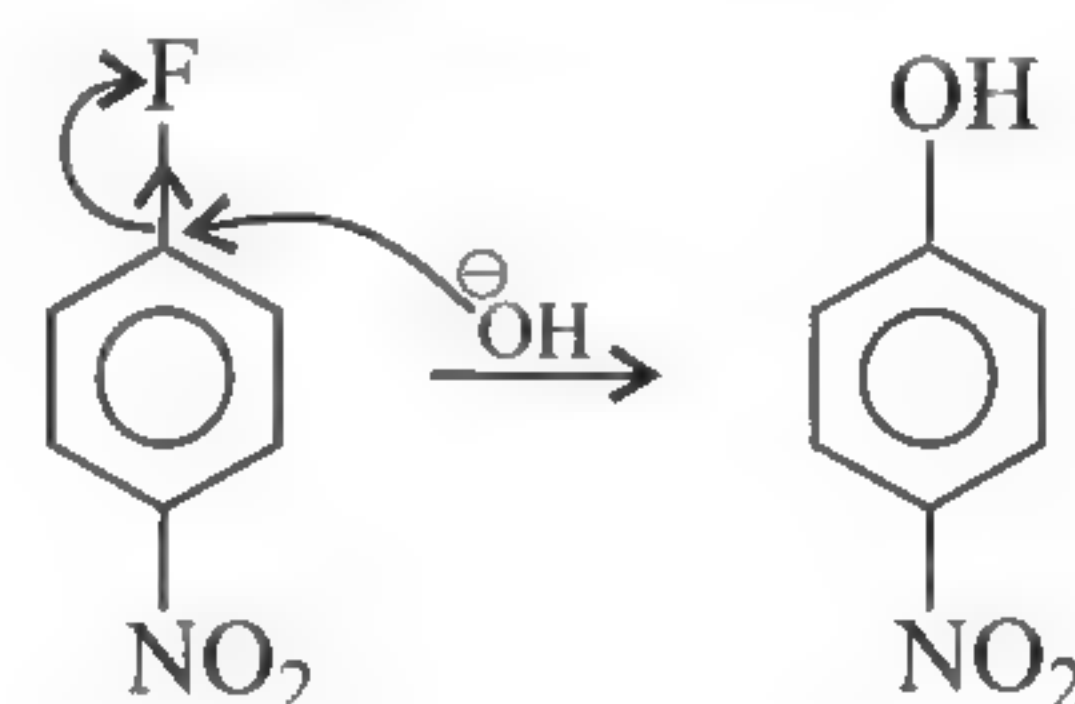


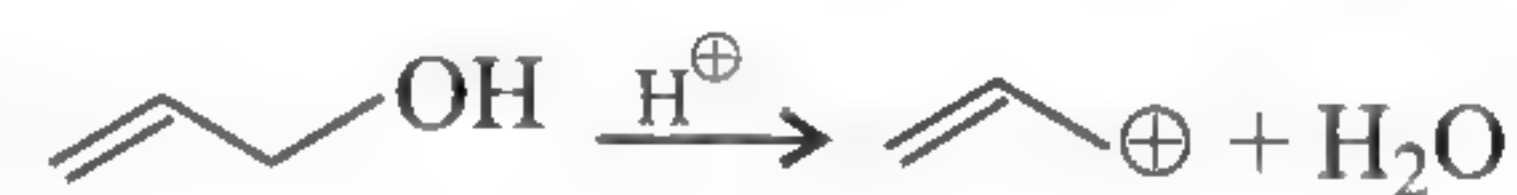
Carbene adds to (=) bond of five-membered ring and simultaneously changes (—NH₂) group in six-membered ring to (—N[⊕]≡C[⊖]) (isocyanide group) (carbylamine reaction).

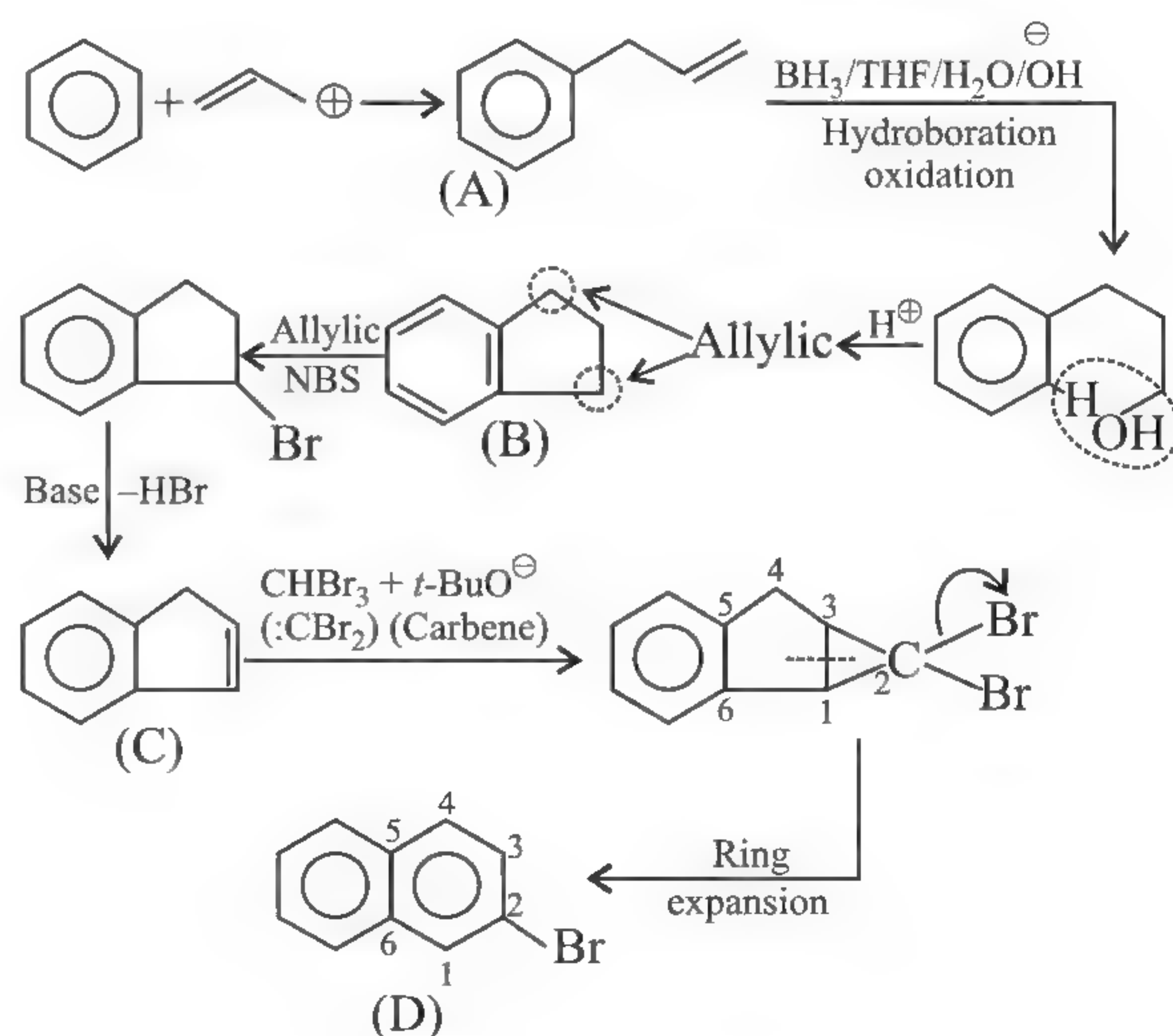


64. (1) ArSN² reactions are favoured by strong EWG, -I effect of F is highest (more EN of F).

(See Illustration 3.17.)

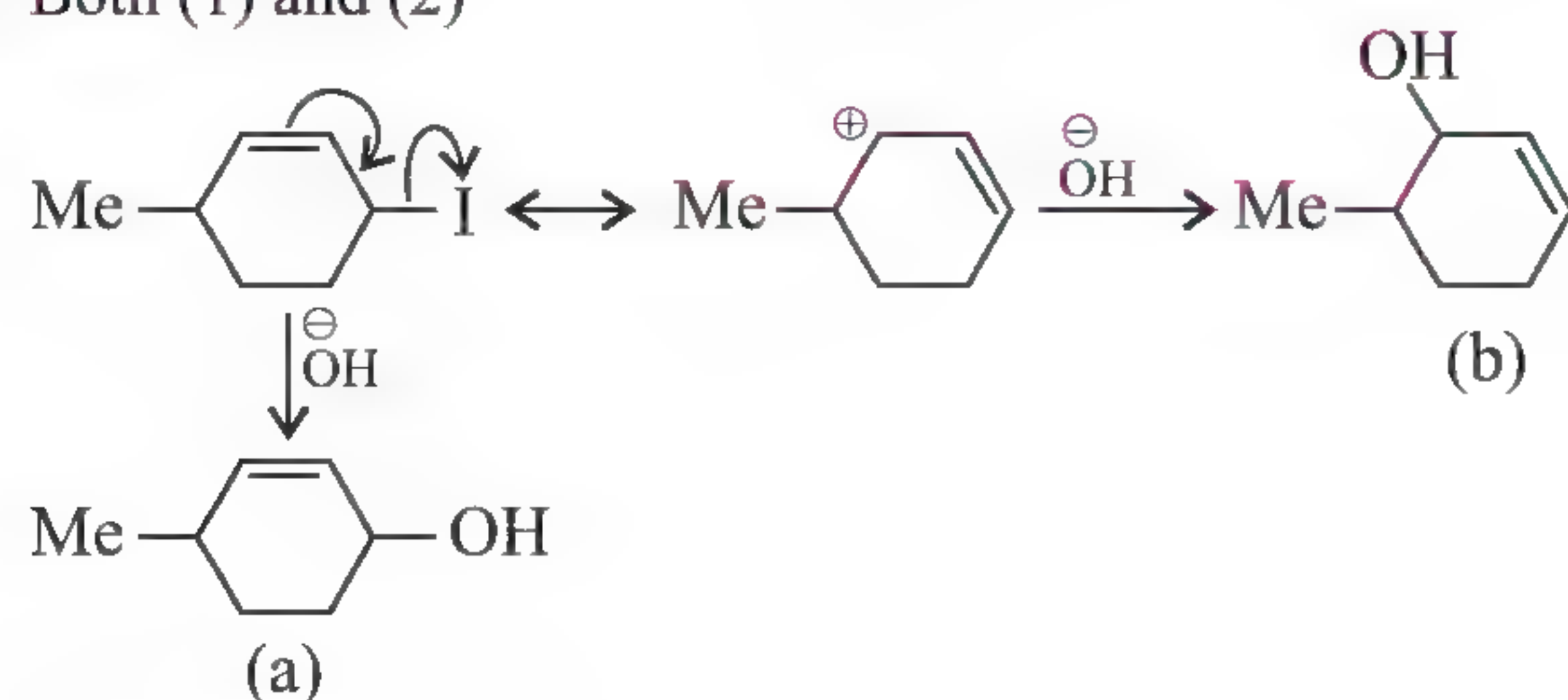


65. (1) 

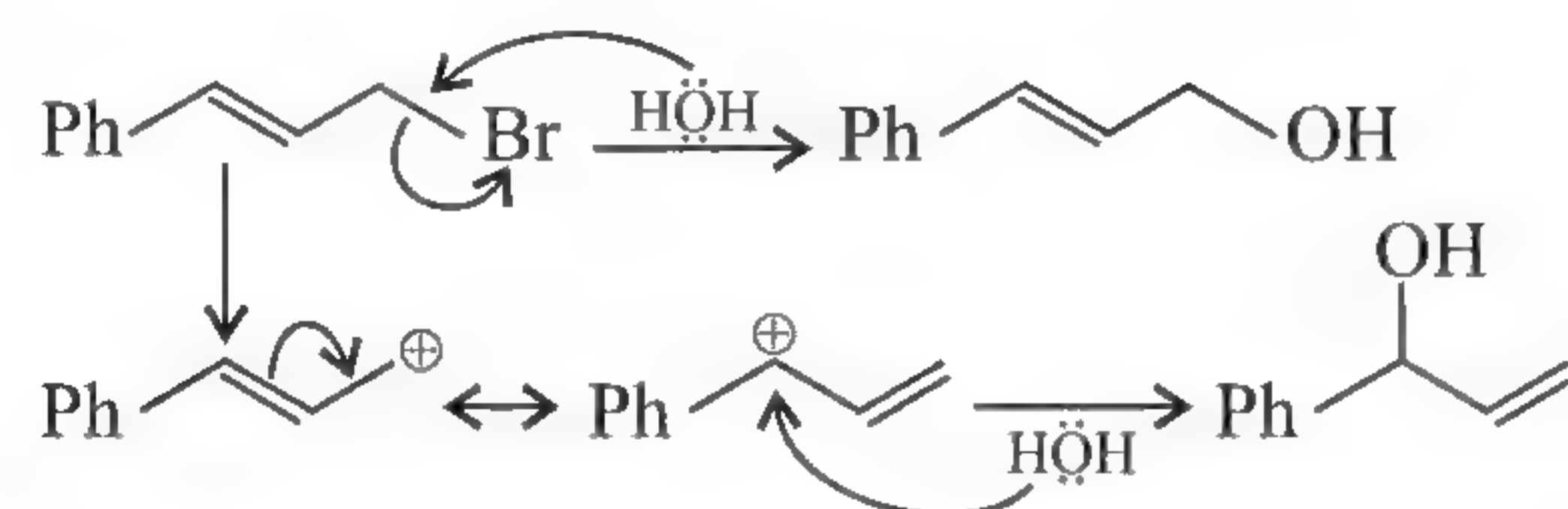


66. (4)

67. (3) Both (1) and (2)

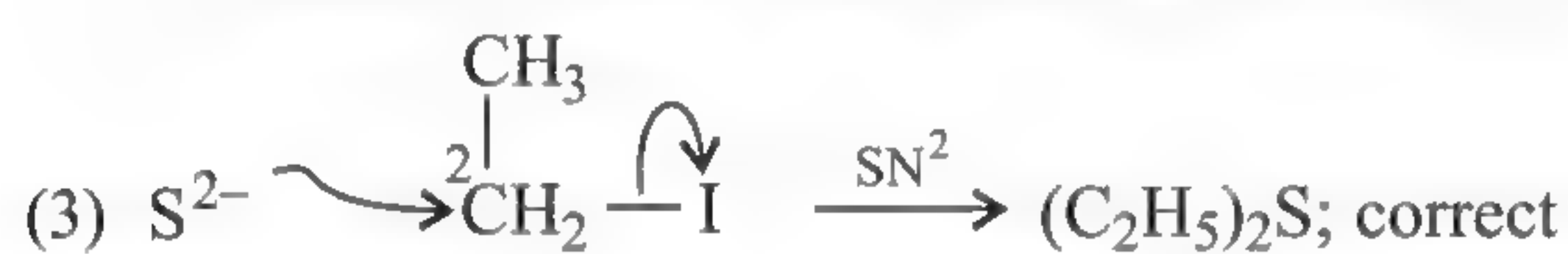


68. (3) [Both (1) and (2)]

69. (2) In basic medium, S_N^2 and in acidic medium, S_N^1 .70. (3) 3°C^\oplus is more stable and hence has less $E_{\text{activation}}$.

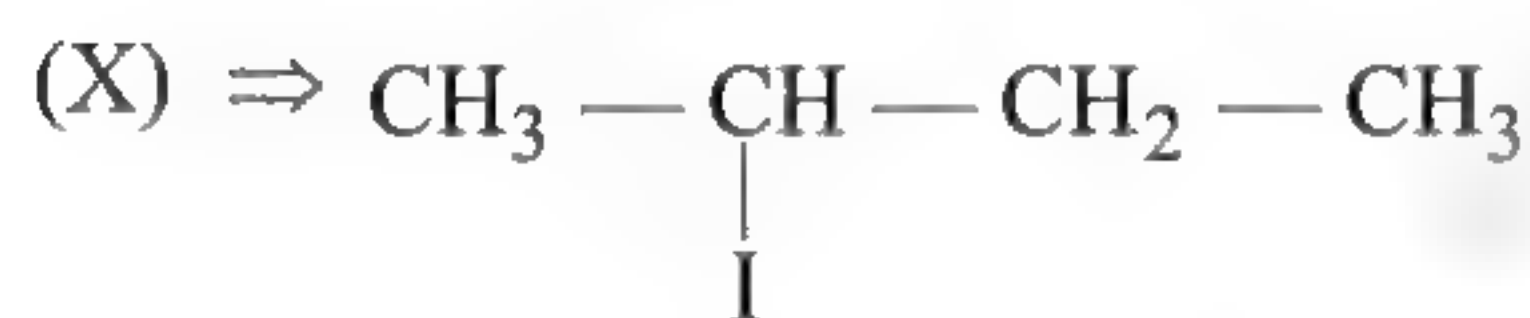
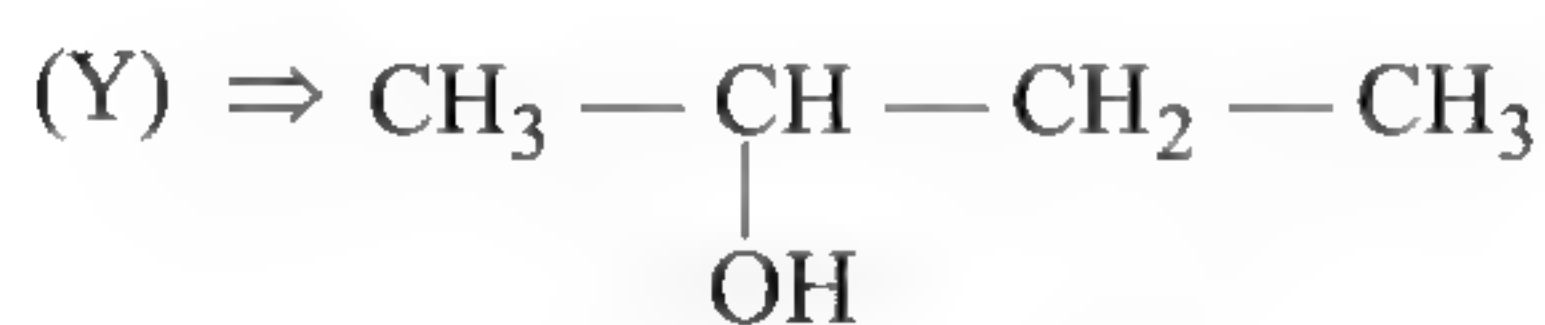
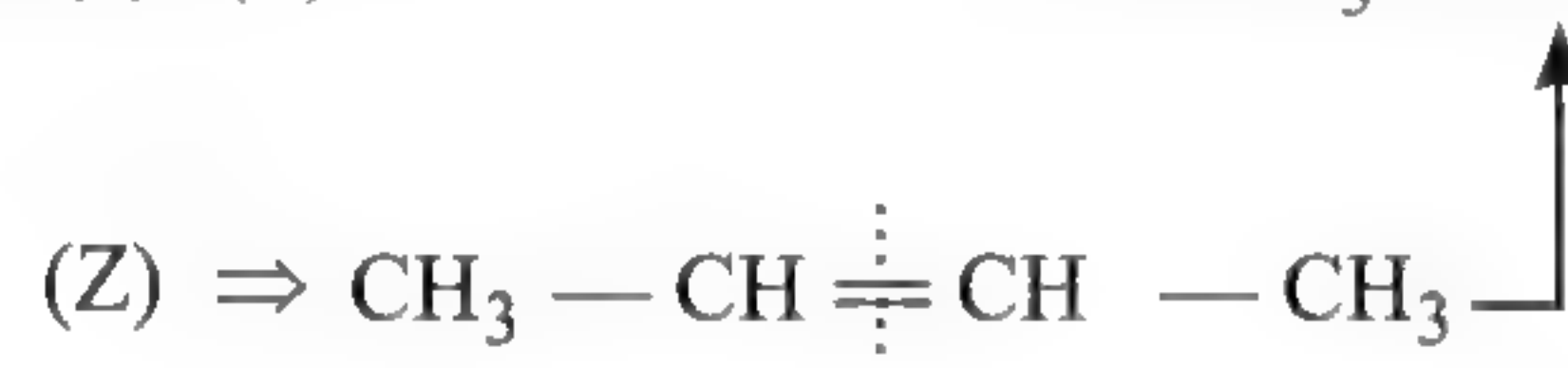
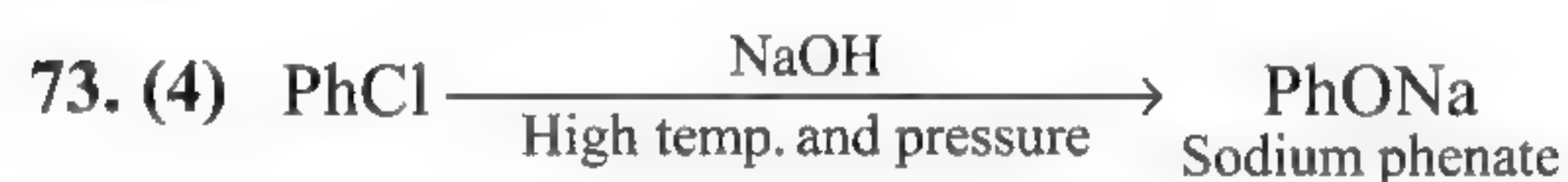
71. (2)

- (1) Wurtz reaction; product is butane, correct.
 (2) Frankland reaction, product would be butane, so wrong.

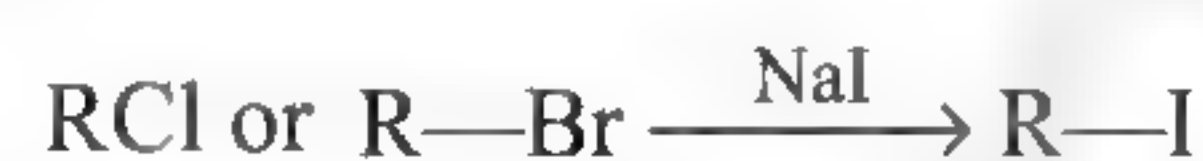


- (4) Finkelstein reaction, correct
 $\text{RBr} + \text{NaI} \rightarrow \text{RI} + \text{NaBr}$

72. (3)



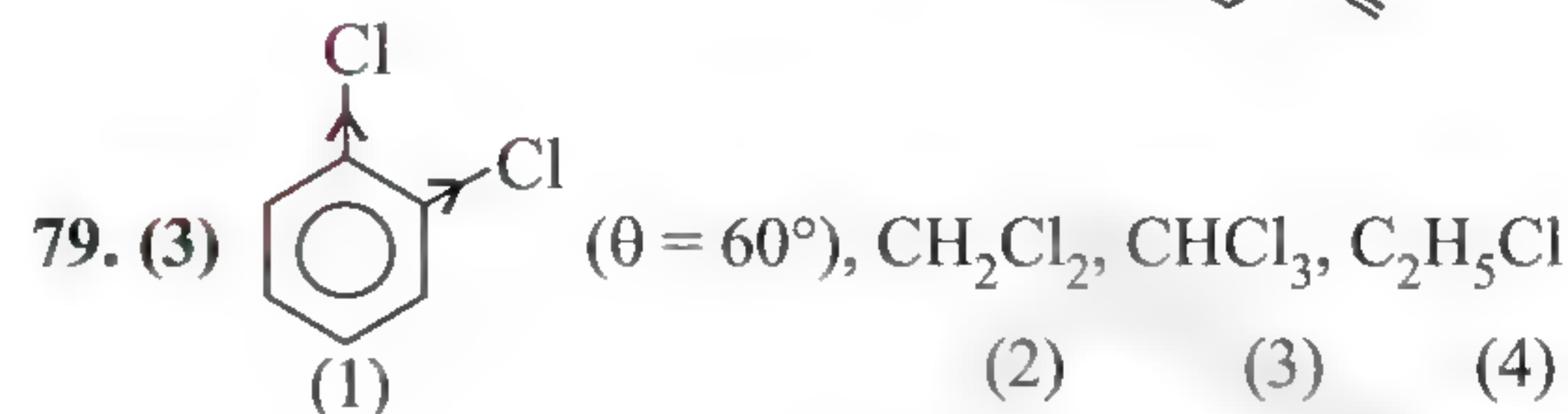
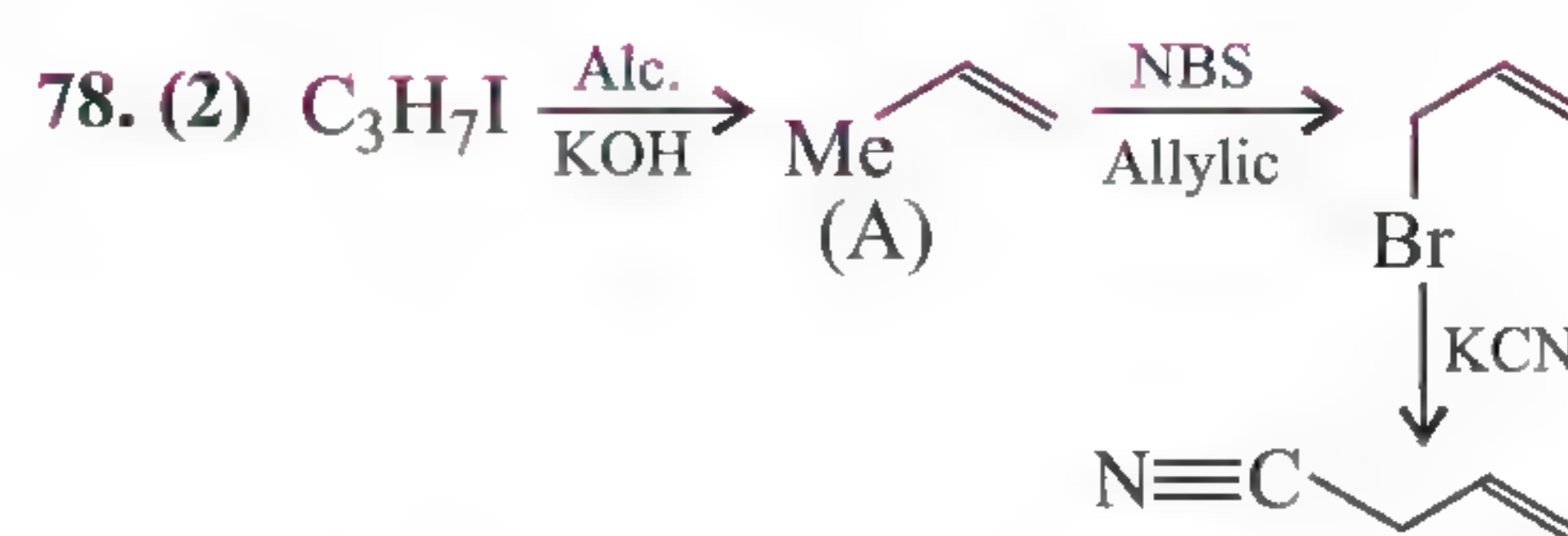
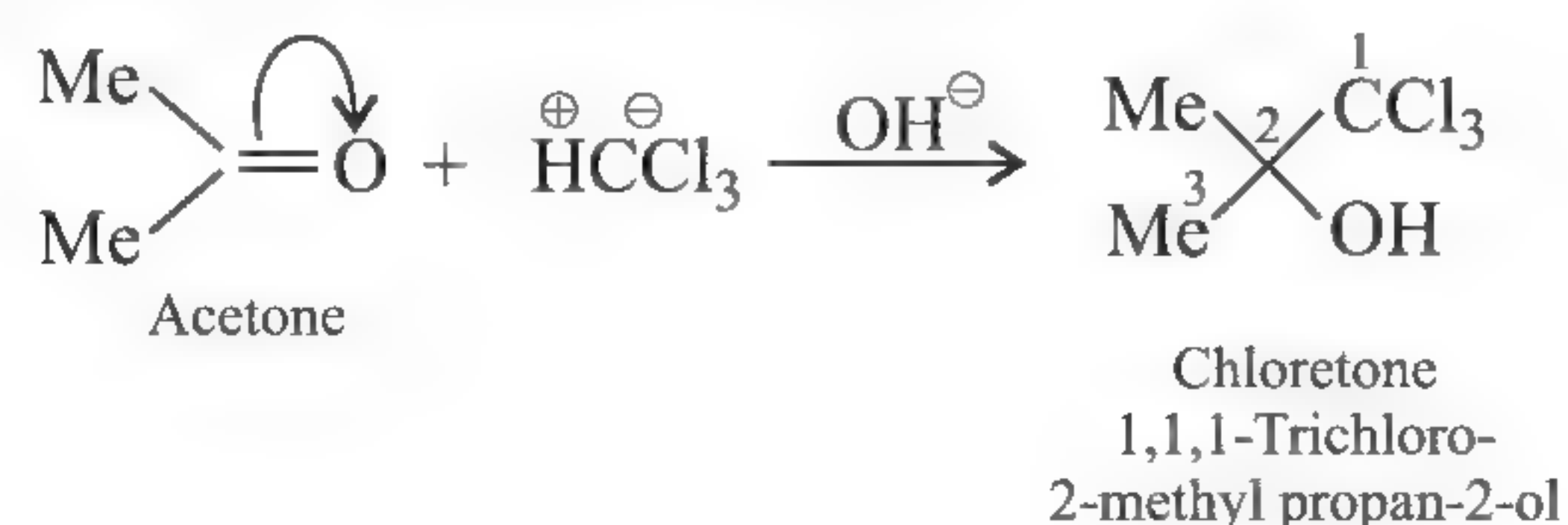
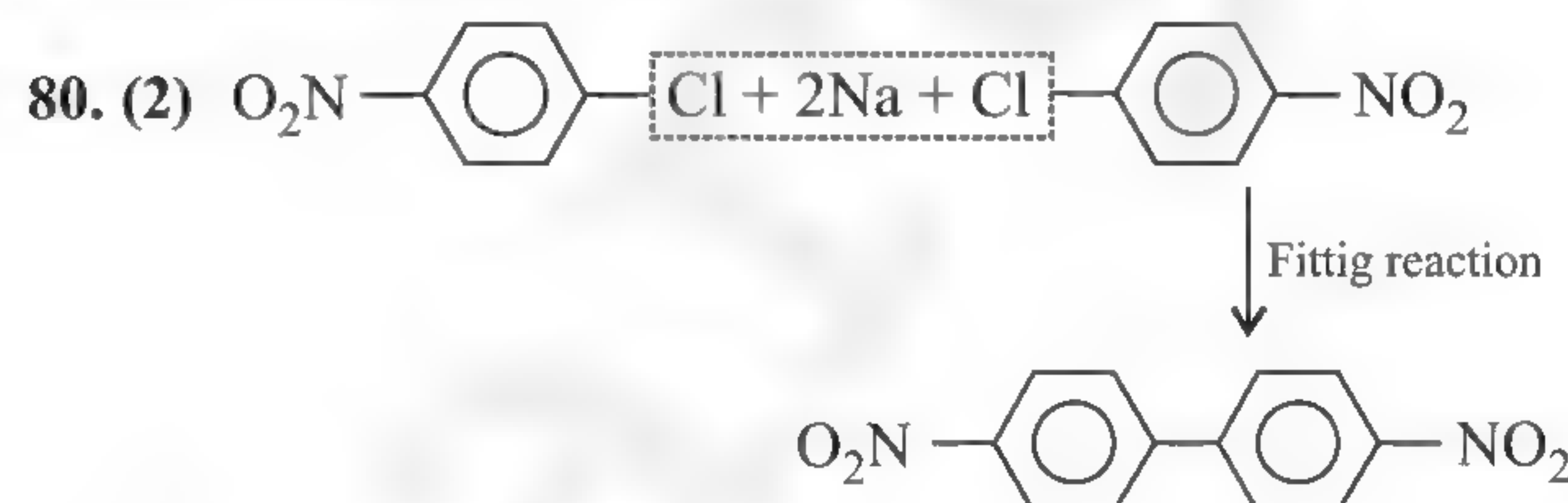
75. (2) Finkelstein reaction



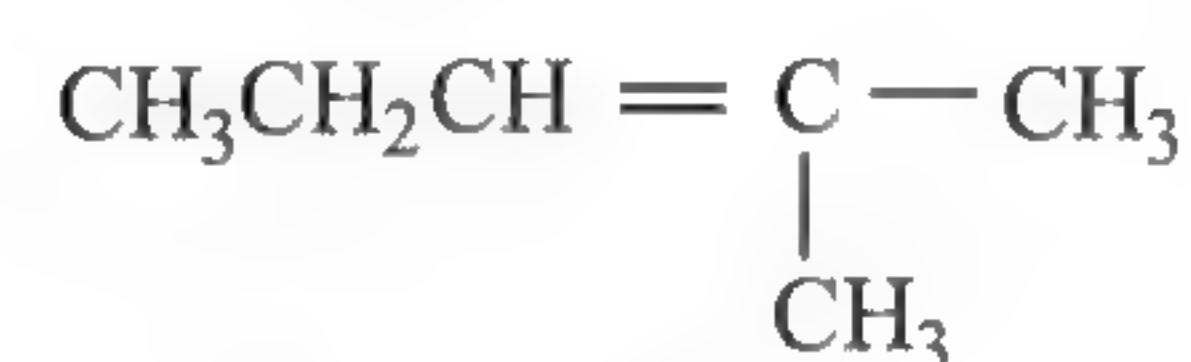
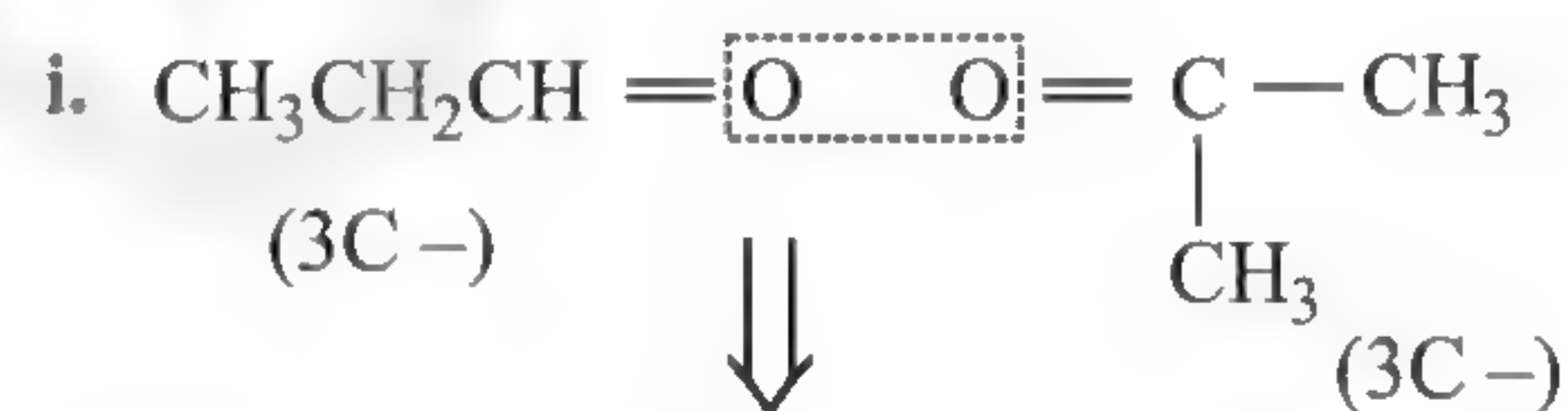
76. (1)

- (1) No reaction
 (2) $\text{CaC}_2 + 2\text{H}_2\text{O} \rightarrow \text{HC} \equiv \text{CH} + \text{Ca}(\text{OH})_2$
 (3) $\text{HC}[\text{I}_3 + 6\text{Ag} + \text{I}_3]\text{CH} \rightarrow \text{HC} \equiv \text{CH} + 6\text{AgI}$
 (4) $\text{HC}[\text{Cl}_3 + 6\text{Ag} + \text{Cl}_3]\text{CH} \rightarrow \text{HC} \equiv \text{CH} + 6\text{AgCl}$

77. (2) Chloretone is used as a hypnotic.

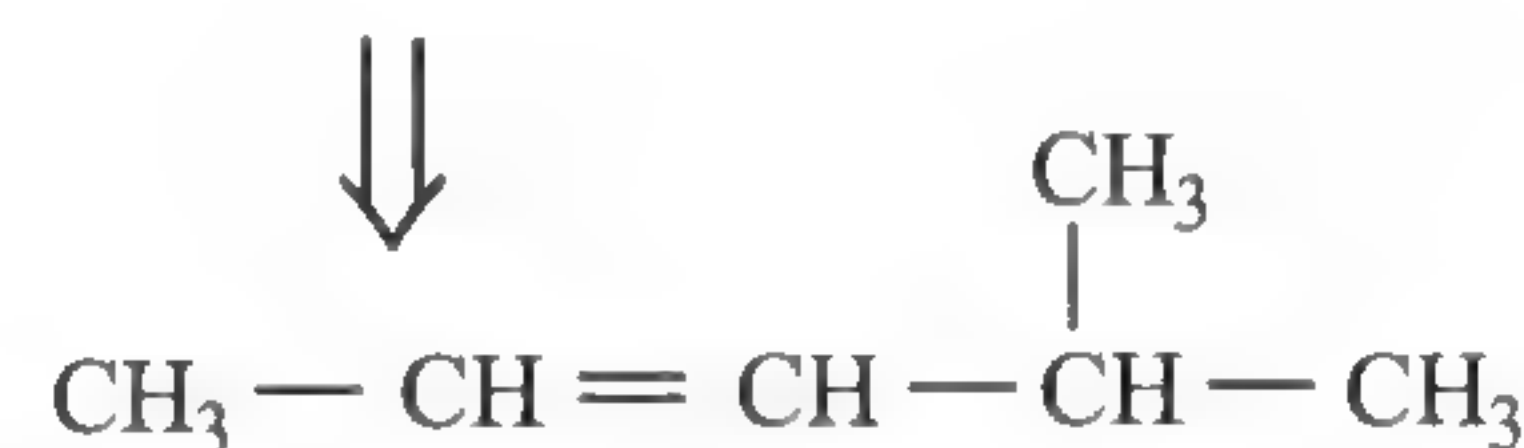
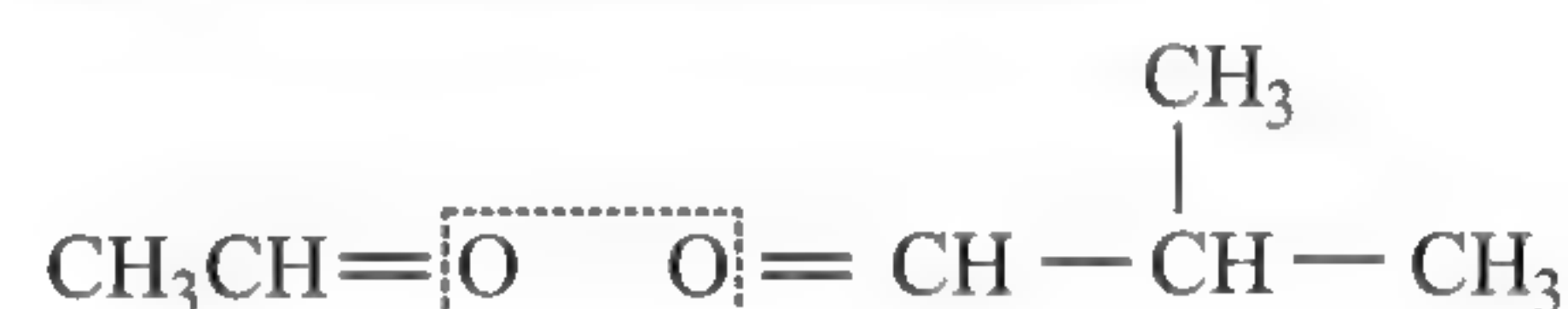
 μ order is: (1) > (4) > (2) > (3).Strongly EWG ($-\text{NO}_2$) group facilitates the reaction.

81. (2) Alkene has six C atoms. Combine two products of ozonolysis containing three C atoms each.

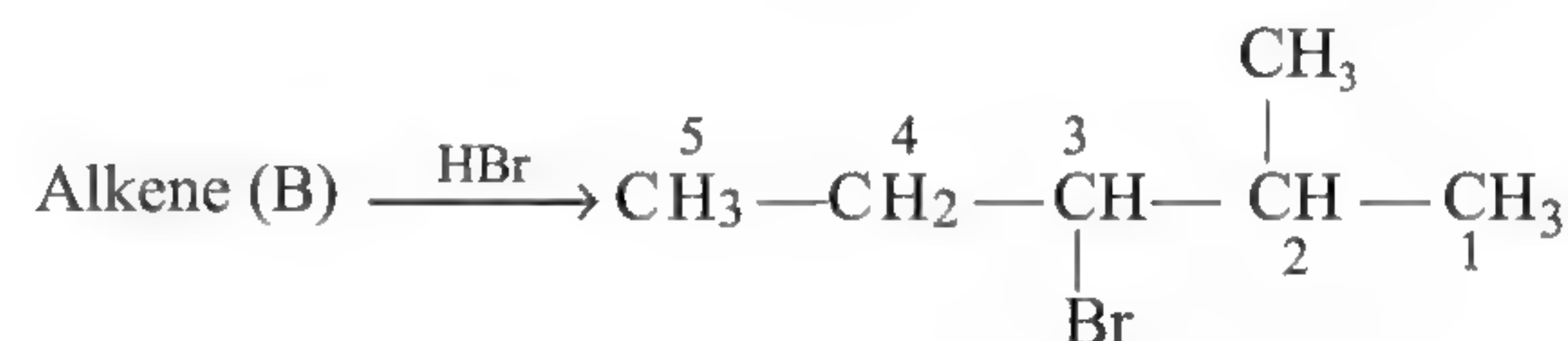


Alkene (A)

ii. Combine two products of ozonolysis containing four C and two C atoms to get another alkene.

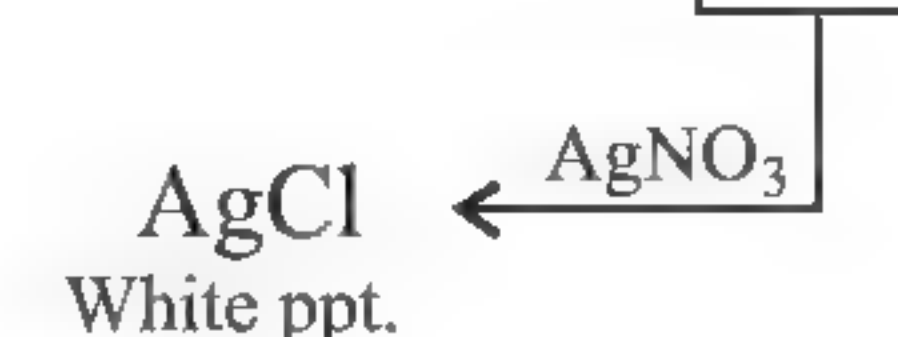
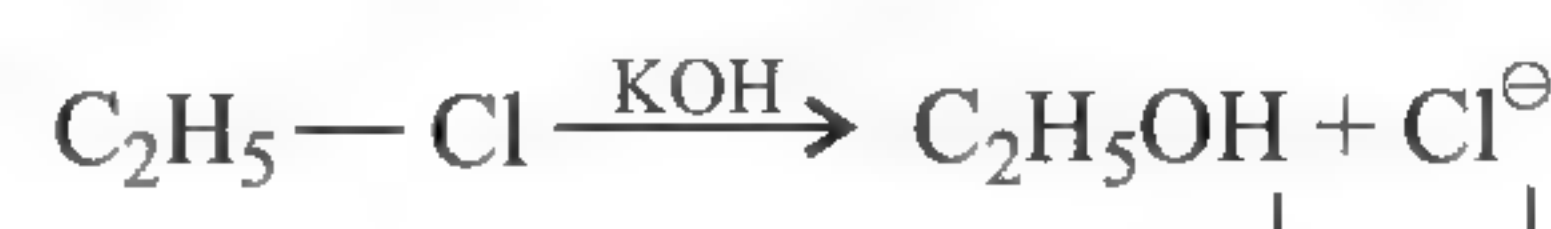


Alkene (B)

Alkene (A) and (B) $\xleftarrow[\text{KOH}]{\text{Alc.}}$ 3-Bromo-2-methyl pentane.

82. (2)

- (1) Lucas reagent will not react with both, since it is a test to distinguish between 1° , 2° , and 3° alcohols.



- (3) AgCl will not react with both.
 (4) HCl/AgCl will not react with both.

83. (1) More the EDG, more reactive is the SE reaction.

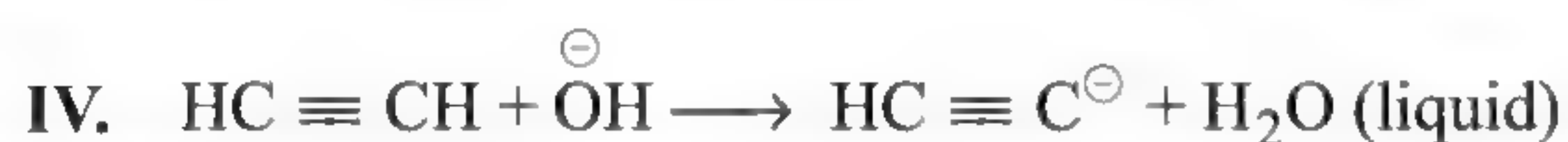
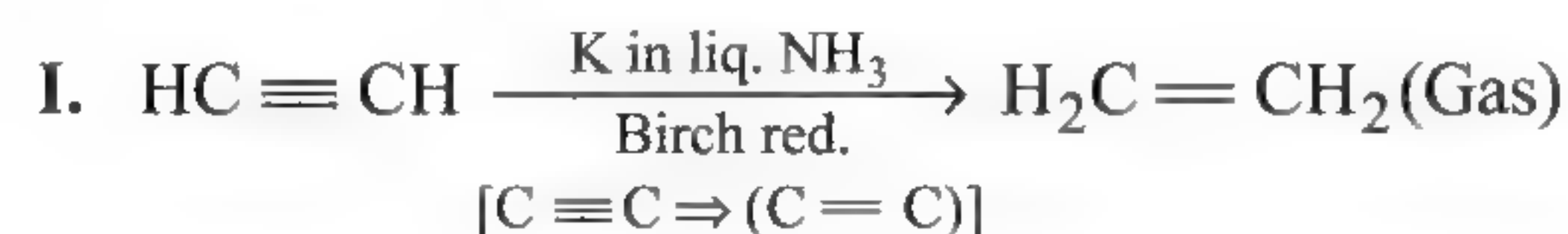
Order of SE = (1) > (4) > (2) > (3).

84. (3) See Section 3.20.

85. (1) More strained the ring, more easily it is cleaved. Three-membered ring is highly strained.

86. (3) Toluene has an allylic group.

87. (1)



88. (4) RCl (alkyl halide) is more reactive than (Ar—I) (arylhalide).

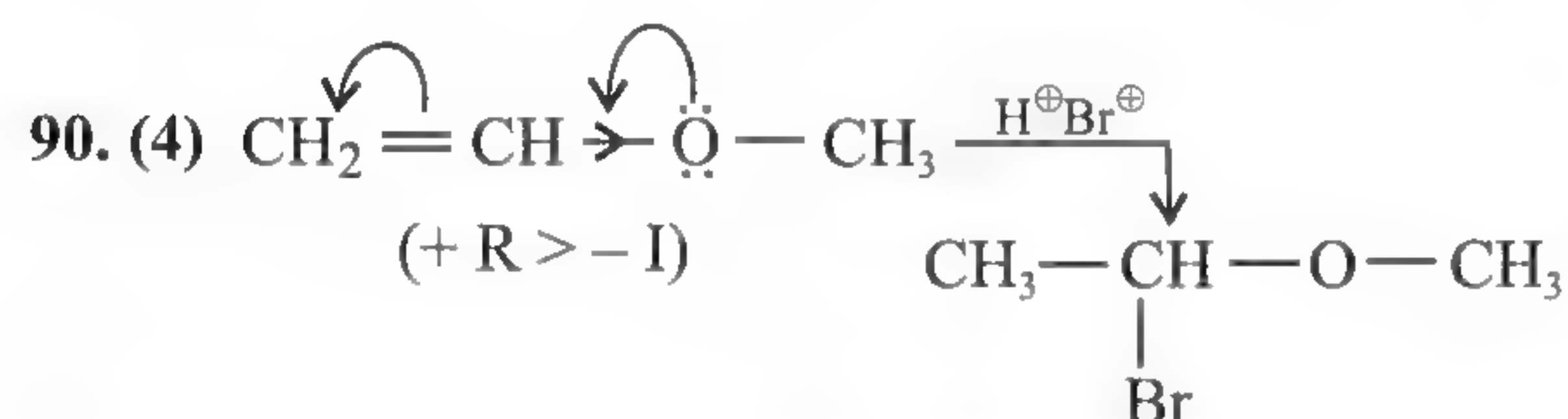
89. (3) Acidic character:

	ACOH	>	PhOH	>	MeOH	>	H ₂ O
pK_a value:	4.75		9.9		15.5		15.74

Basic and nucleophilic characters are same because of same nucleophilic centre.

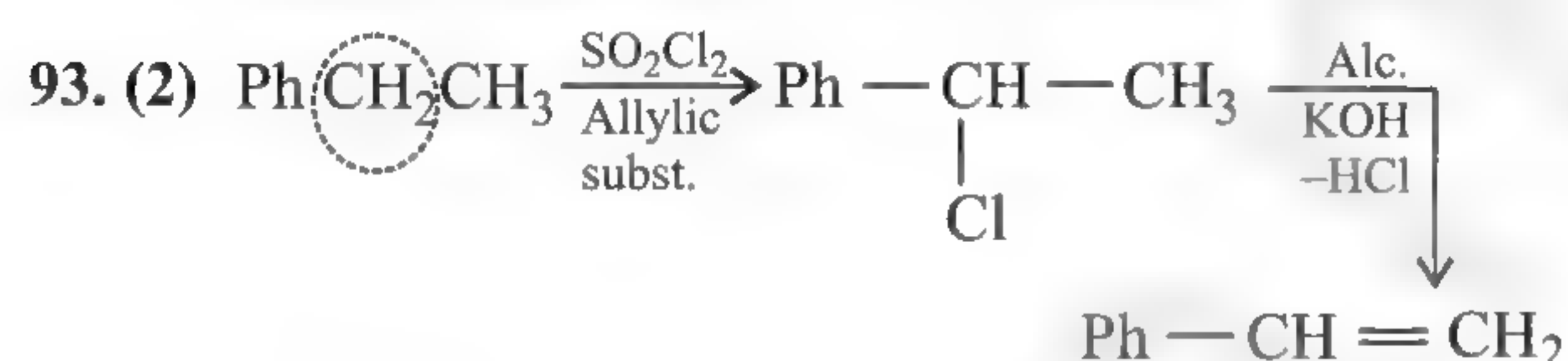
Nucleophilic order:

AcO ⁻	<	PhO ⁻	<	MeO ⁻	<	OH ⁻
(B)	<	(A)	<	(D)	<	(C)



91. (1) In (II) and (V), the dipole vectors are cancelled, so there is zero dipole moment.

92. (2) More the number of C atoms (high molecular mass) and straight chain (large surface area), higher the boiling points.



94. (2) See Section 3.3.

95. (4) ArSN reaction occurs in (2), (3) and (4) since they have EWG (–NO₂) at *o*- and *p*-position w.r.t. leaving (–Br) group.

Carbanion intermediate is obtained on attack of OH with one nitro group at *o/p* shows light yellow, two nitro at *o/p* shows purple colour and three nitro at *o/p* shows red colour.

96. (3) Br (r) is having EWG (Br) at *o*- & *p*-position. So it will undergo ArSN with NaOH.

Br (p) is having EWG (Br) at *p*- and *m*-position.

97. (4) Refer to Illustration 3.13.

98. (1) The leaving group 'Br' is same. ArSN reactivity is determined by EWG. More the EW power, more is the reactivity. The EW power of –CHO > –COOH.

More the EDG, lesser is the reactivity.

The ED power of –OCH₃ (+ R and –I) > –CH₃ (+I and H.C.).

Hence the order is : IV > I > II > III

99. (2) The leaving group 'F' is same and is present at *o*- position of EWG (–NO₂) group. More the EDG, lesser is the reactivity.

The ED power of:

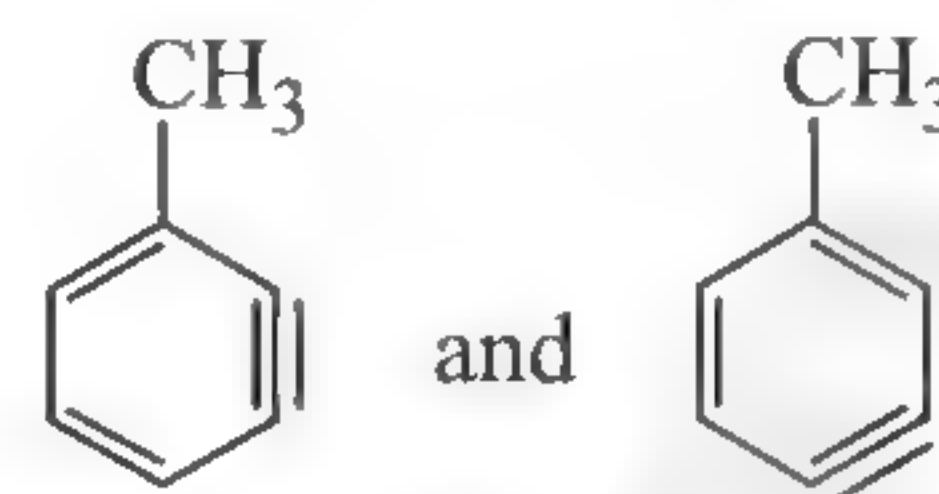
–CH₃ (+ I and 3 H.C.) > –C₂H₅ (+I and 2 H.C.)

> –CH(CH₃)₂ (+I, one H.C.) > –C(CH₃)₃ (+I, No H.C.)

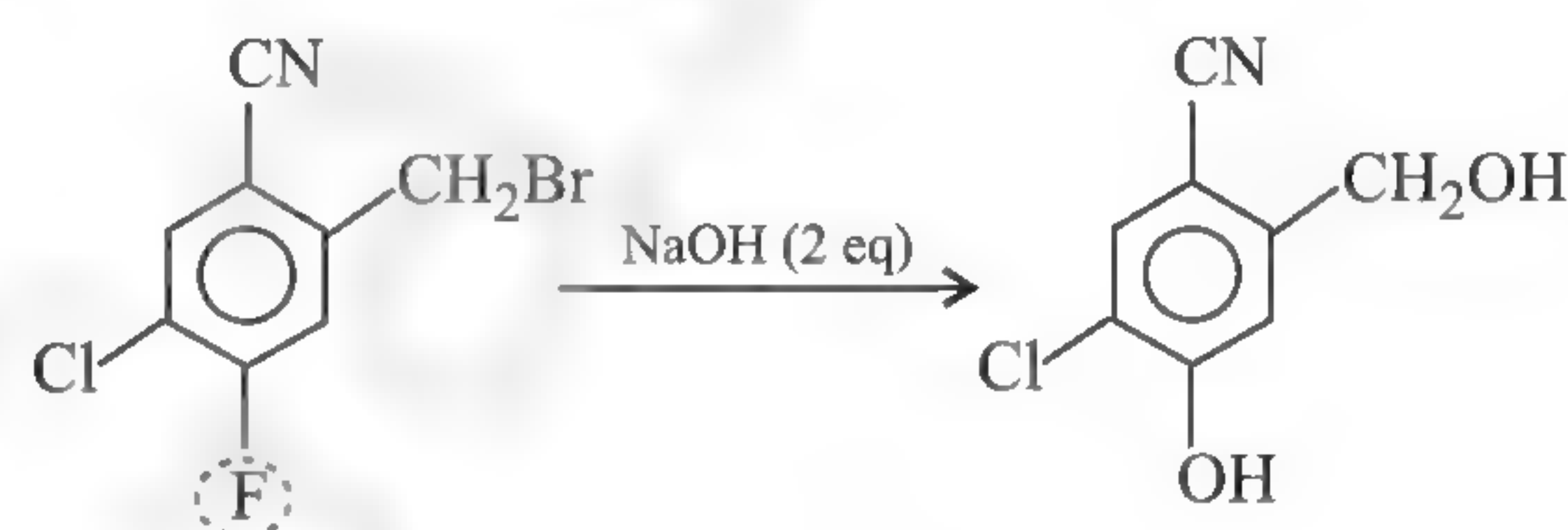
Thus the order is: IV > III > II > I

100. (2) Refer to Illustration 3.4 (b).

In (2) two types of benzyne are obtained.



101. (2)



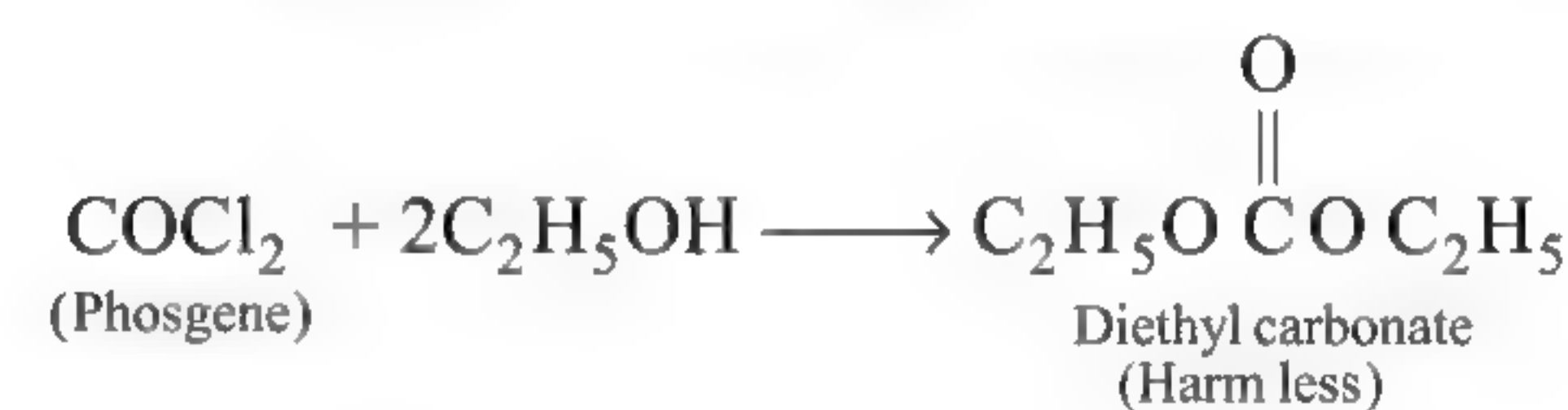
The leaving group order is: F > Cl > Br > I.

The 'F' atom is *p*-position w.r.t. EWG (–CN) whereas the 'Cl' atom is at *m*-position w.r.t. (–CN) group. The second equivalent of NaOH further reacts with Br.

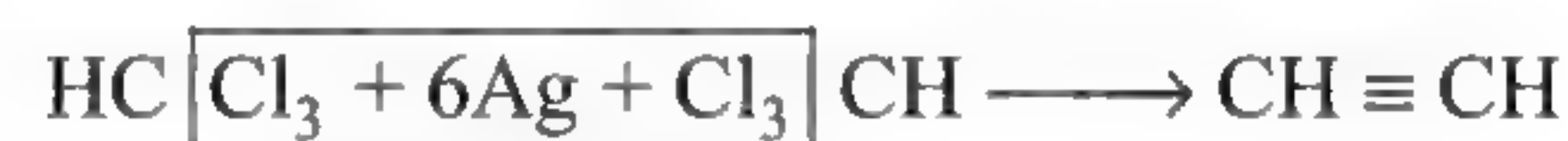
102. (1) Correct (1): $\text{CS}_2 + 3\text{Cl}_2 \xrightarrow{\text{AlCl}_3} \text{CCl}_4 + \text{S}_2\text{Cl}_2$.

Correct (2): CCl₄ is called pyrene and is used as fire extinguisher.

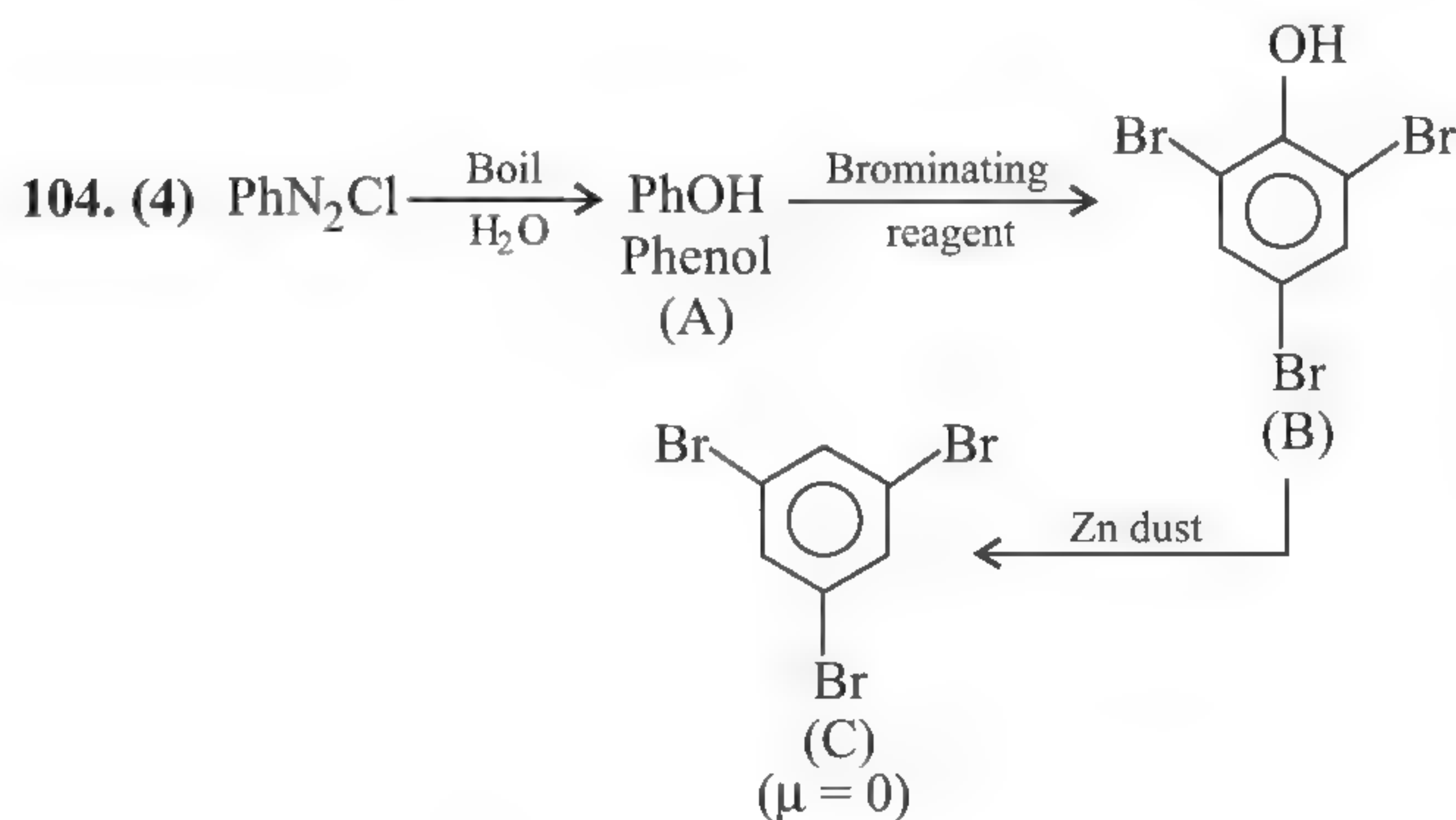
Correct (3): It is removed by adding ethanol.



Correct (4): It gives ethyne.



103. (2) Refer to section 3.4.4 to 3.4.6.

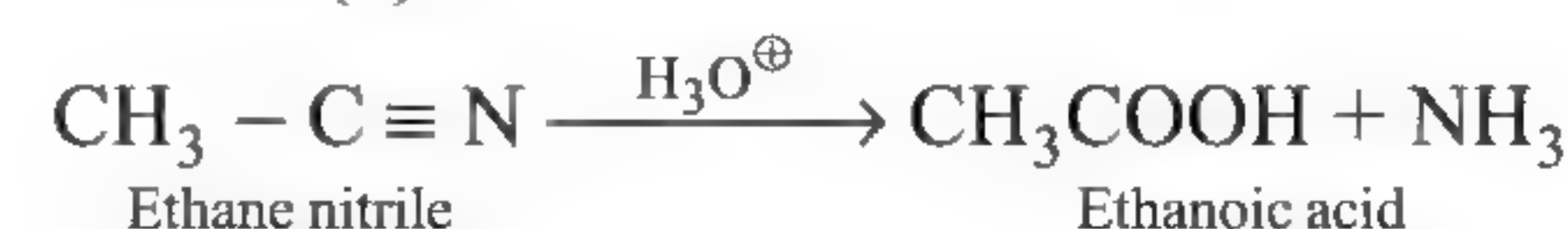


Statement (1), (2) and (3) are correct.

Correct (4), $\mu_B > \mu_C$.

105. (3) Refer to section 3.7.1 to 3.7.3.

Correct (1):



∴ Reactivity factor (RF) of chlorination
 = Relative reactivity of 3° H-atoms ×
 Number of 3° H-atoms (Probability factor)
 = $5.0 \times 1.0 = 5$.

(ii) Compound (C) is obtained by chlorination of nine equivalent of 1° H-atoms.

∴ Reactivity factor of chlorination is compound (C)
 = Relative reactivity of 1° H-atom × Number of 1° H-atom.
 = $1 \times 9 = 9$

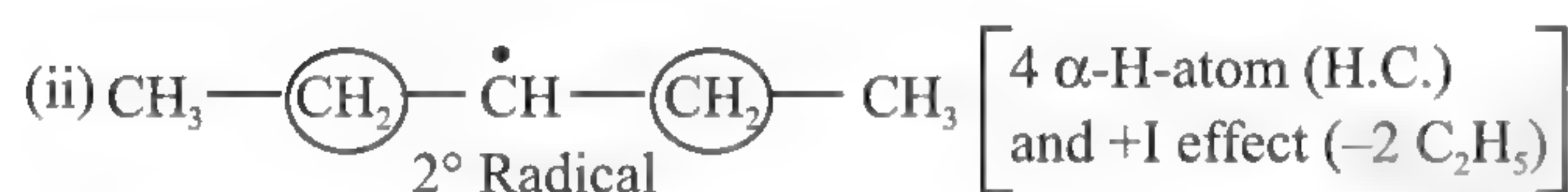
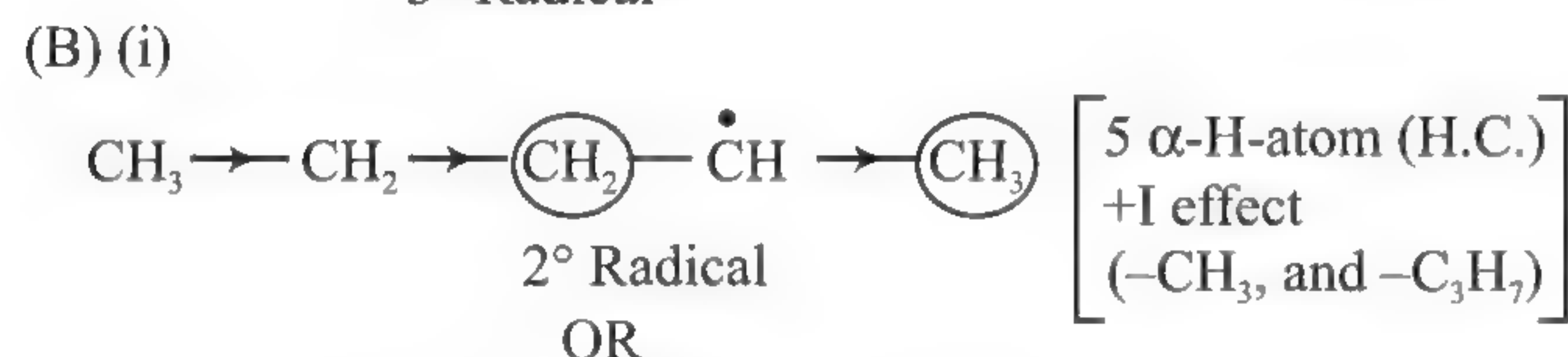
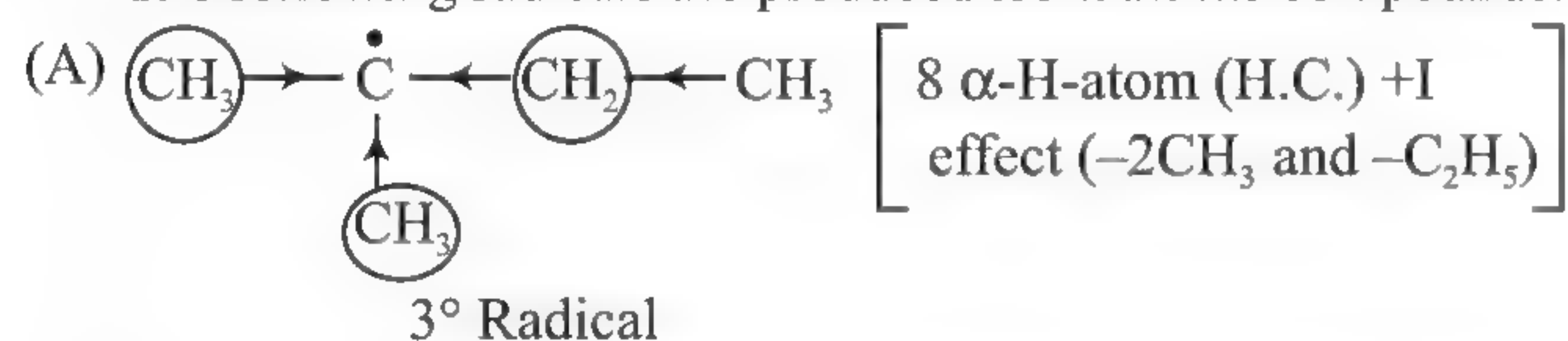
Total relative factor = $5 + 9 = 14$

$$\therefore \% \text{ of B} = \frac{5}{14} \times 100 = 35.7\%$$

$$\% \text{ of C} = \frac{9}{14} \times 100 = 64.3\%$$

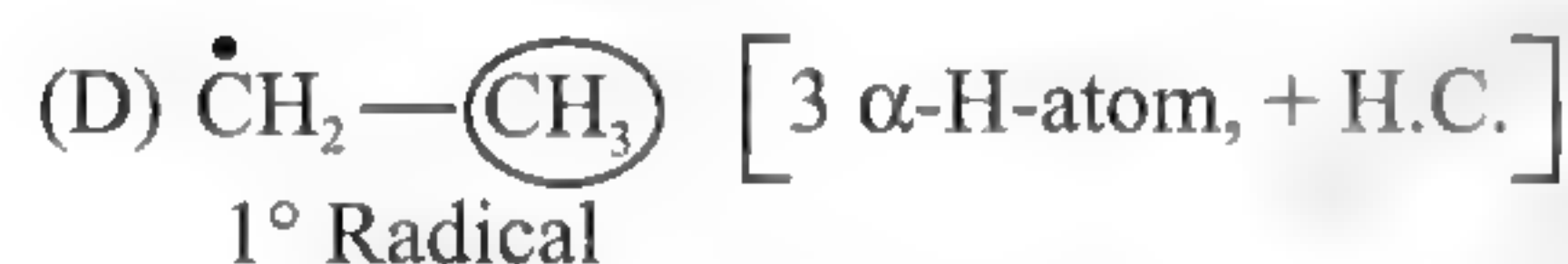
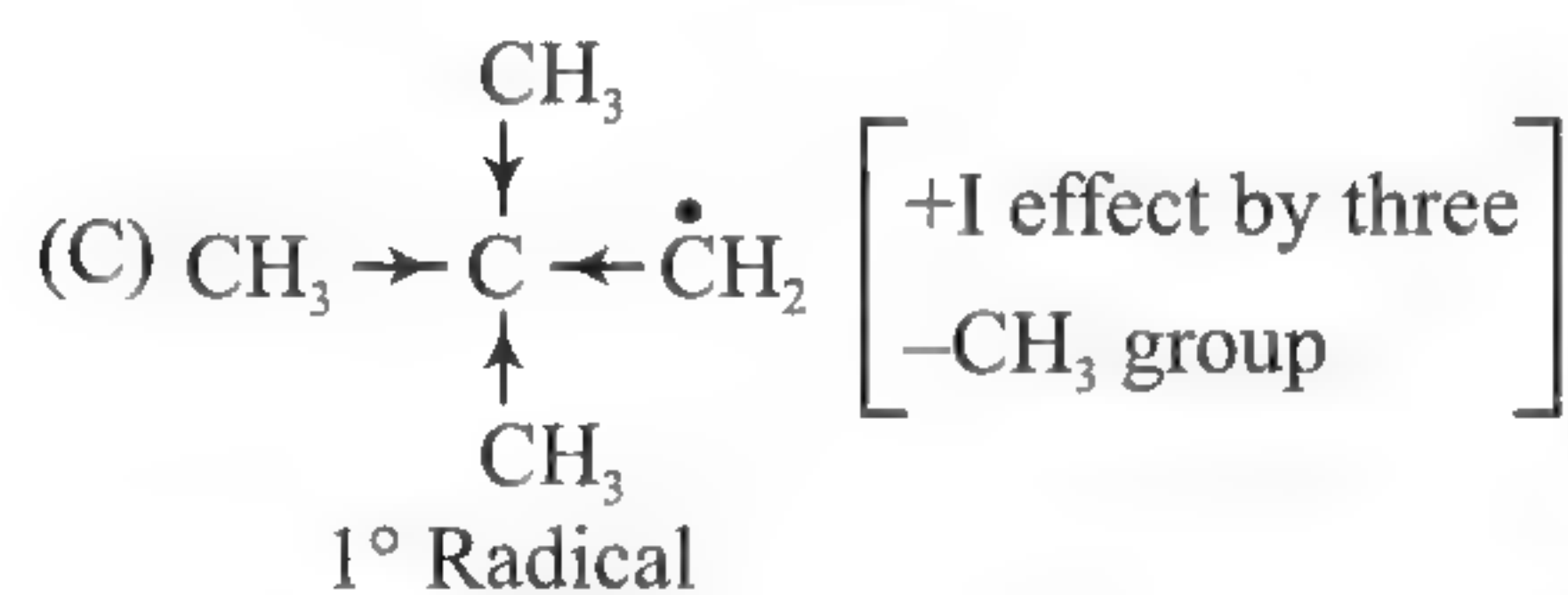
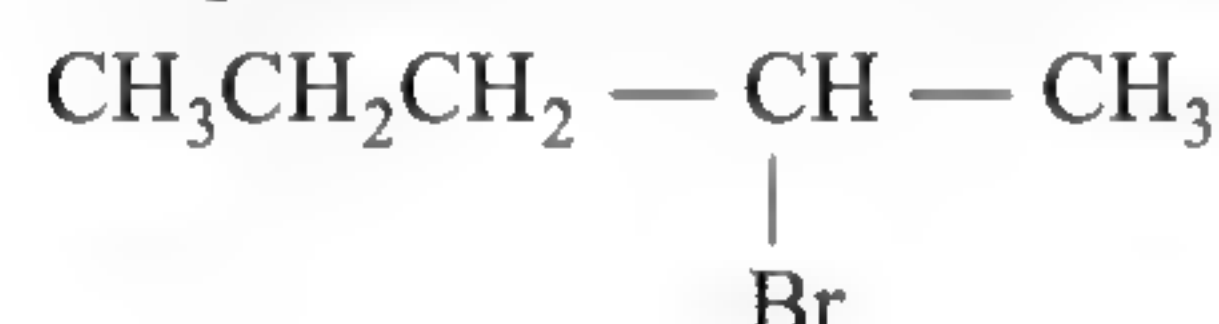
118. (1) Reactivity of photochemical chlorination or bromination \propto stability of free radical ($3^\circ > 2^\circ > 1^\circ$)

The following radicals are produced from all the compounds.



Radical (i) > Radical (ii)

The product in B is from radical in (i), i.e.,

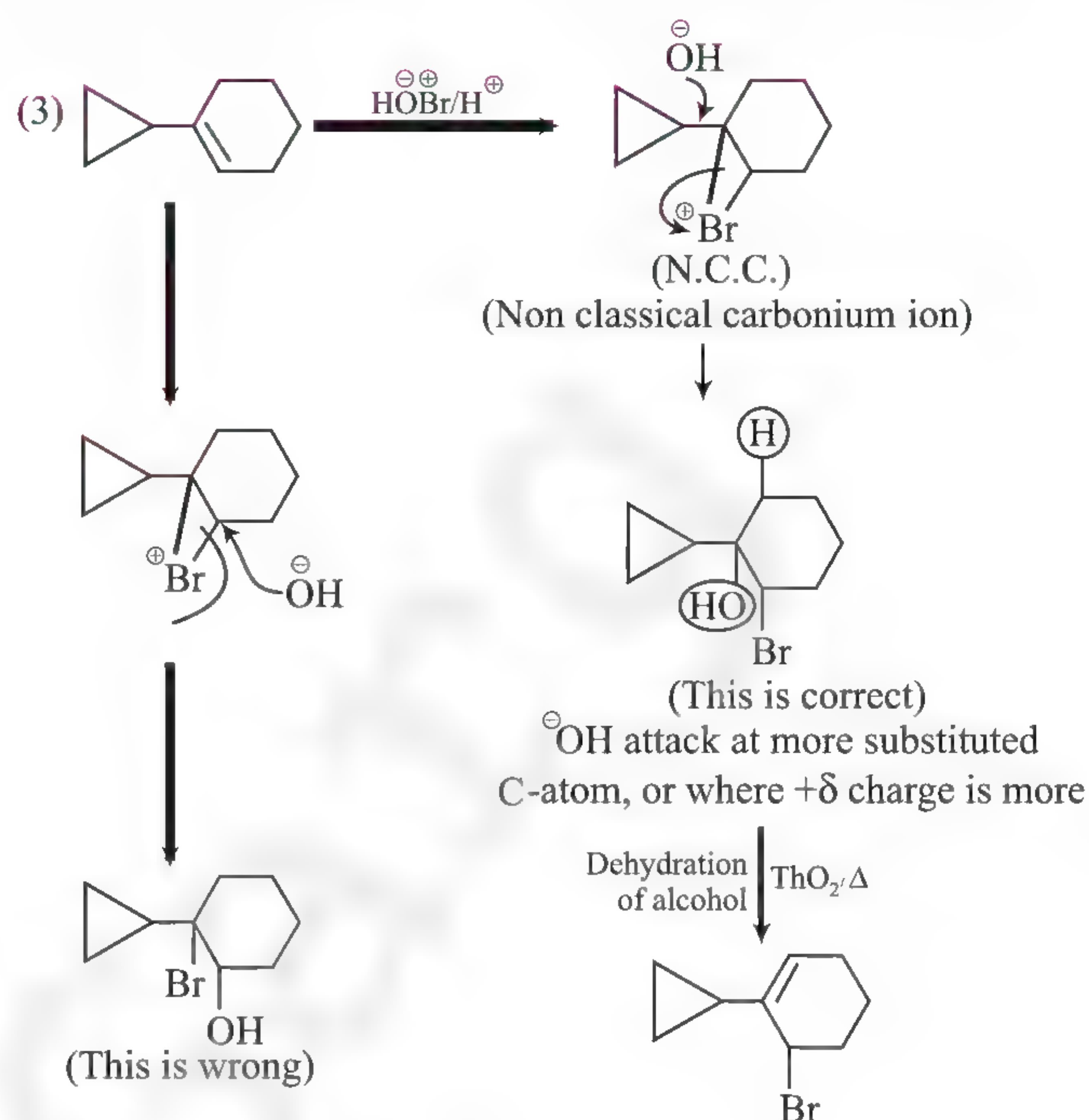
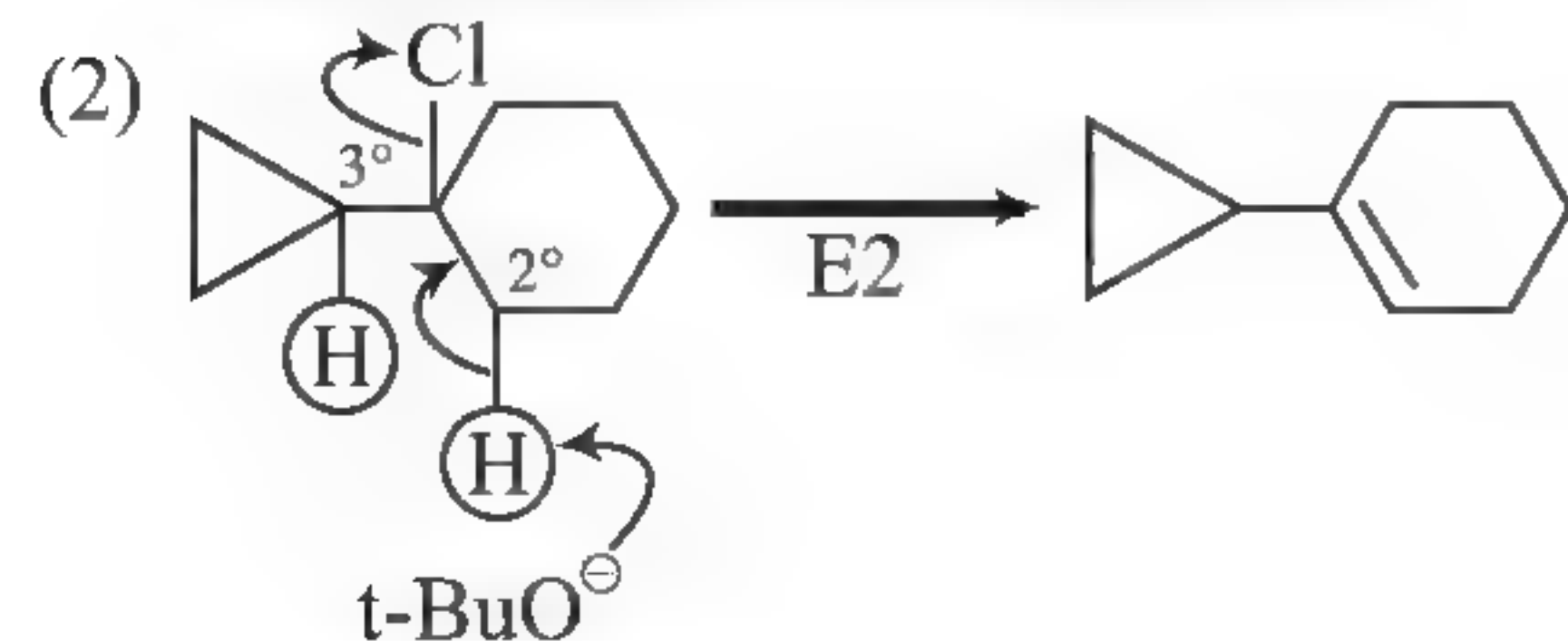
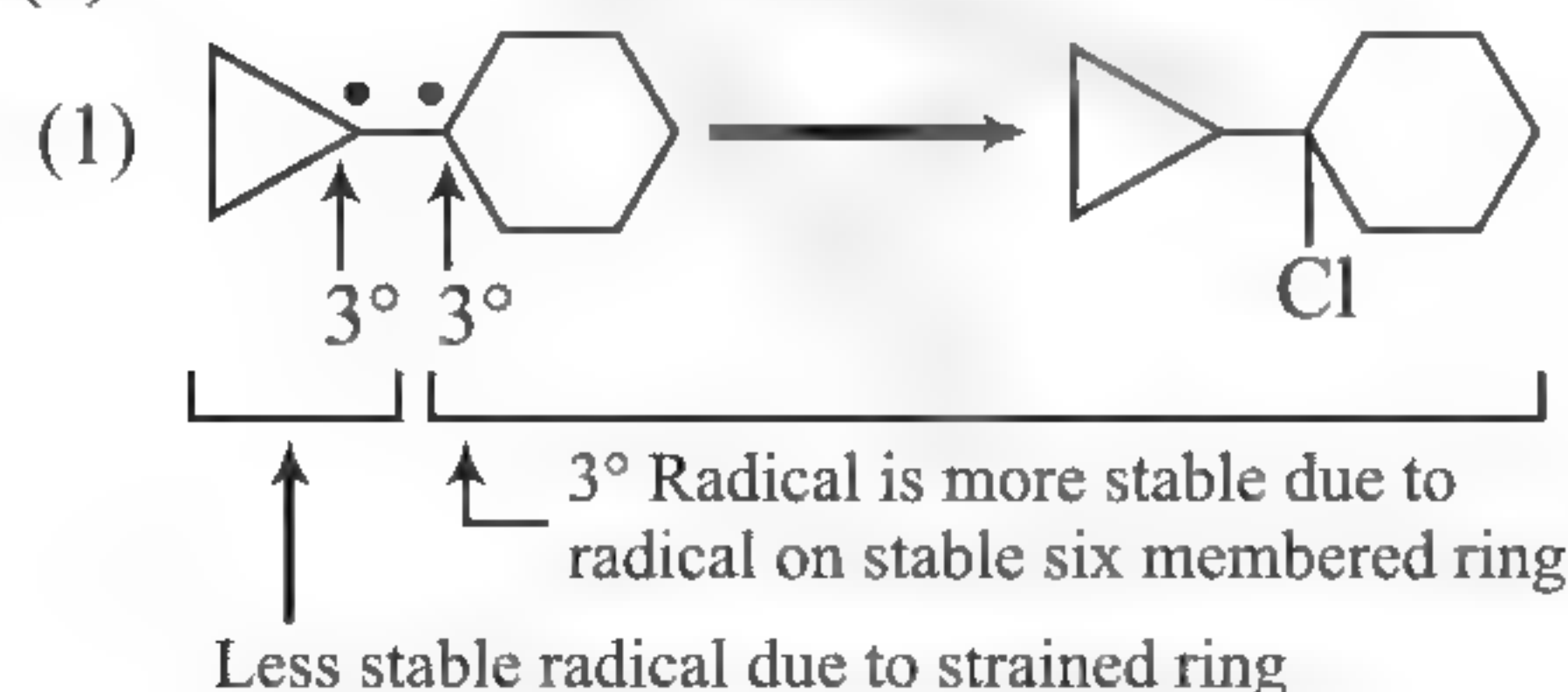


Radical produced from (C) is more stable than produced from (D), because + I effect by three ($-\text{CH}_3$) groups is more dominant than H.C. effect by $3\alpha\text{-H-atom}$.

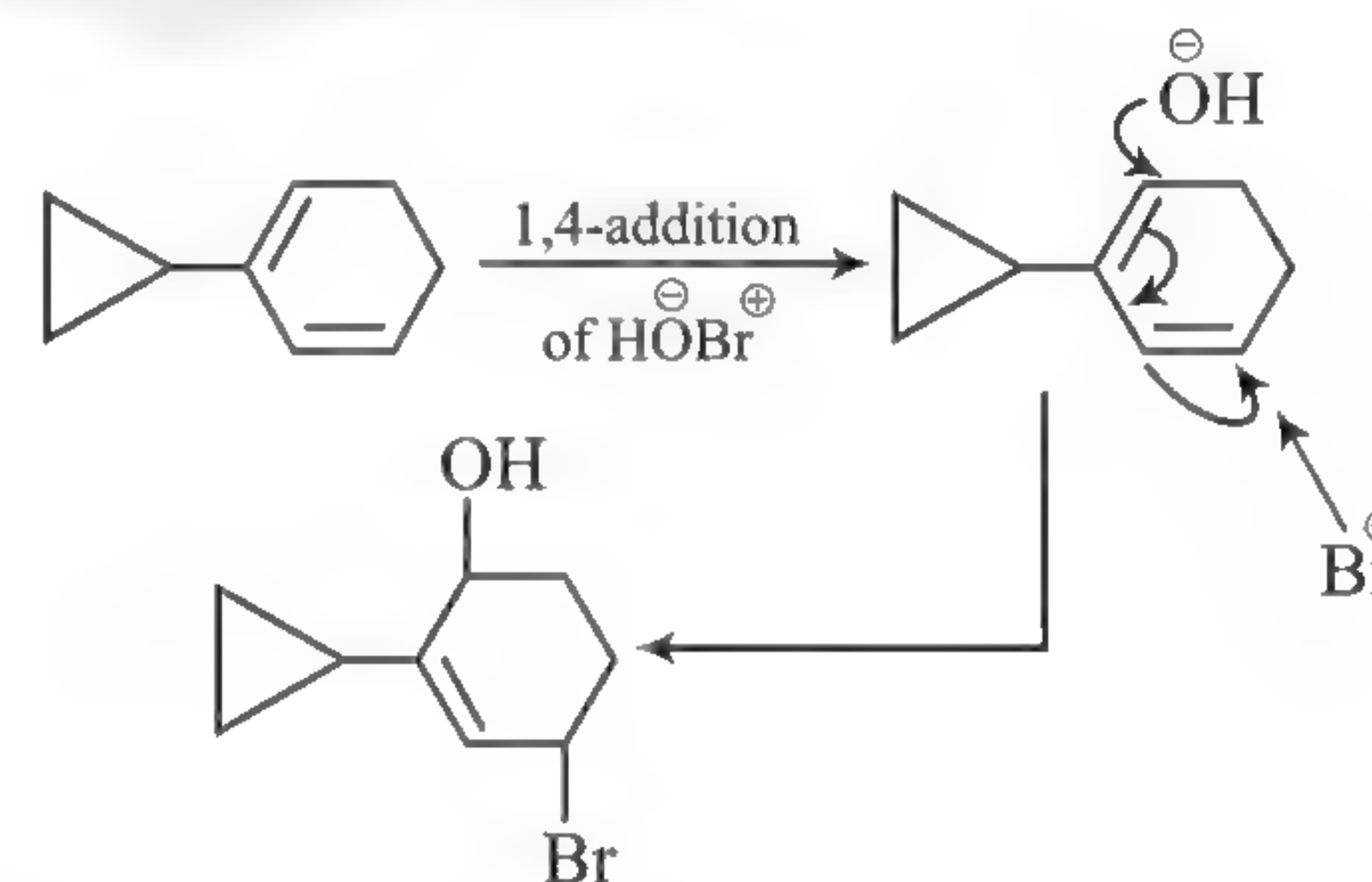
Thus reactivity order:

$A > B > C > D$

119. (4)



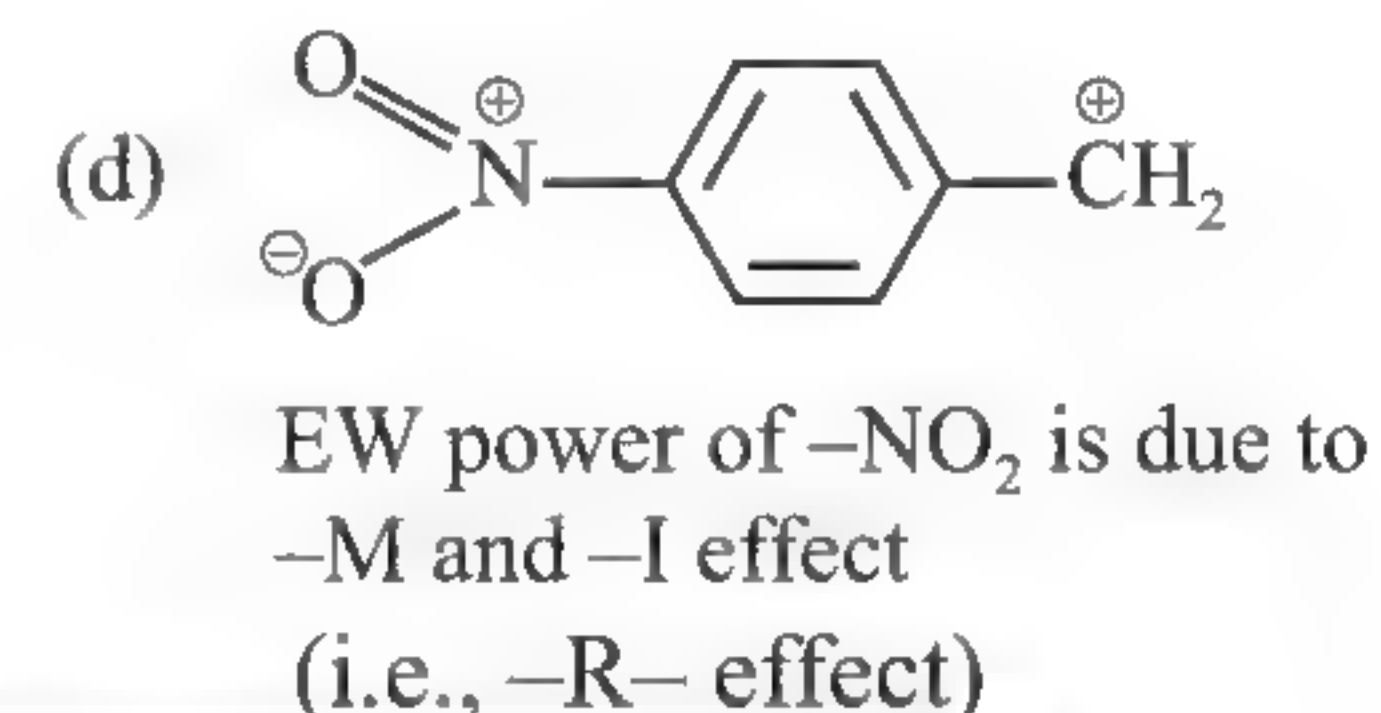
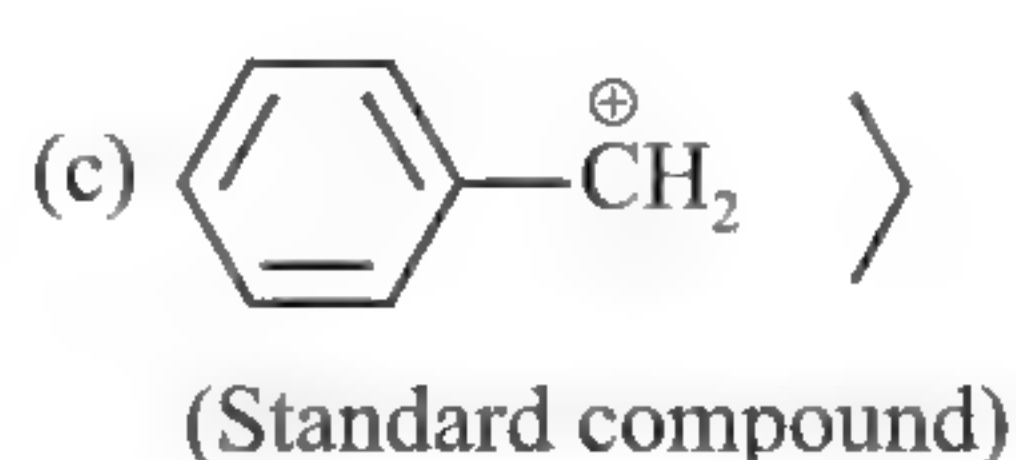
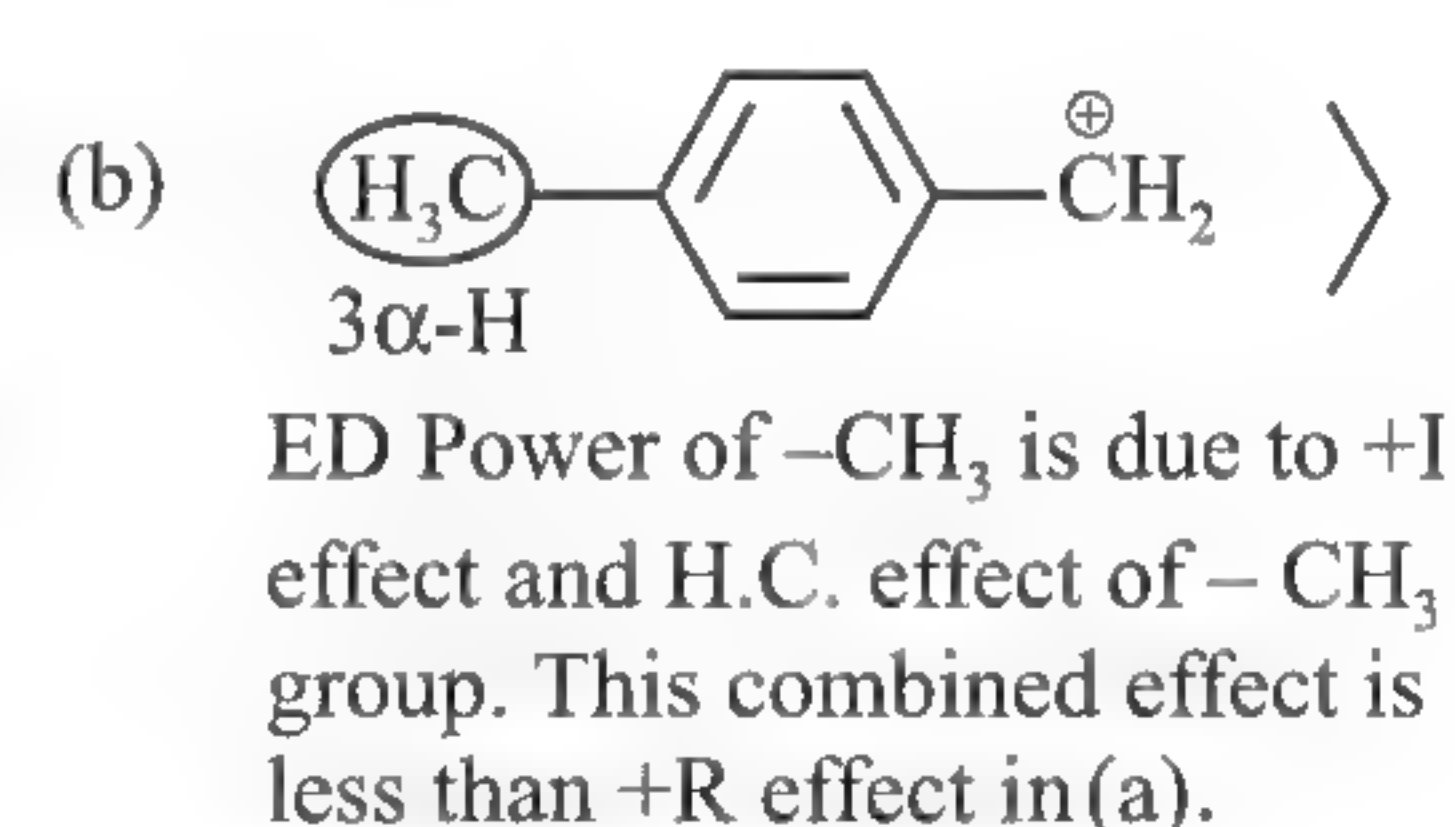
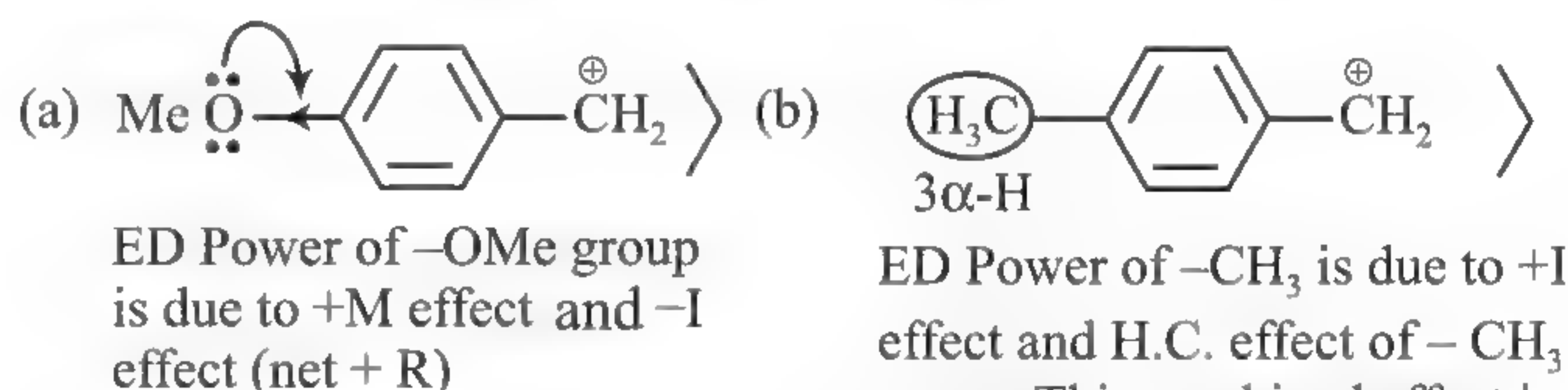
(4) This reaction is correct.



120. (1) $a > b > c > d$

Benzyl carbocation is stabilised by EDG (e.g., $-\text{OCH}_3$ and $-\text{CH}_3$ group) and destabilised by EWG (e.g., $-\text{NO}_2$ group).

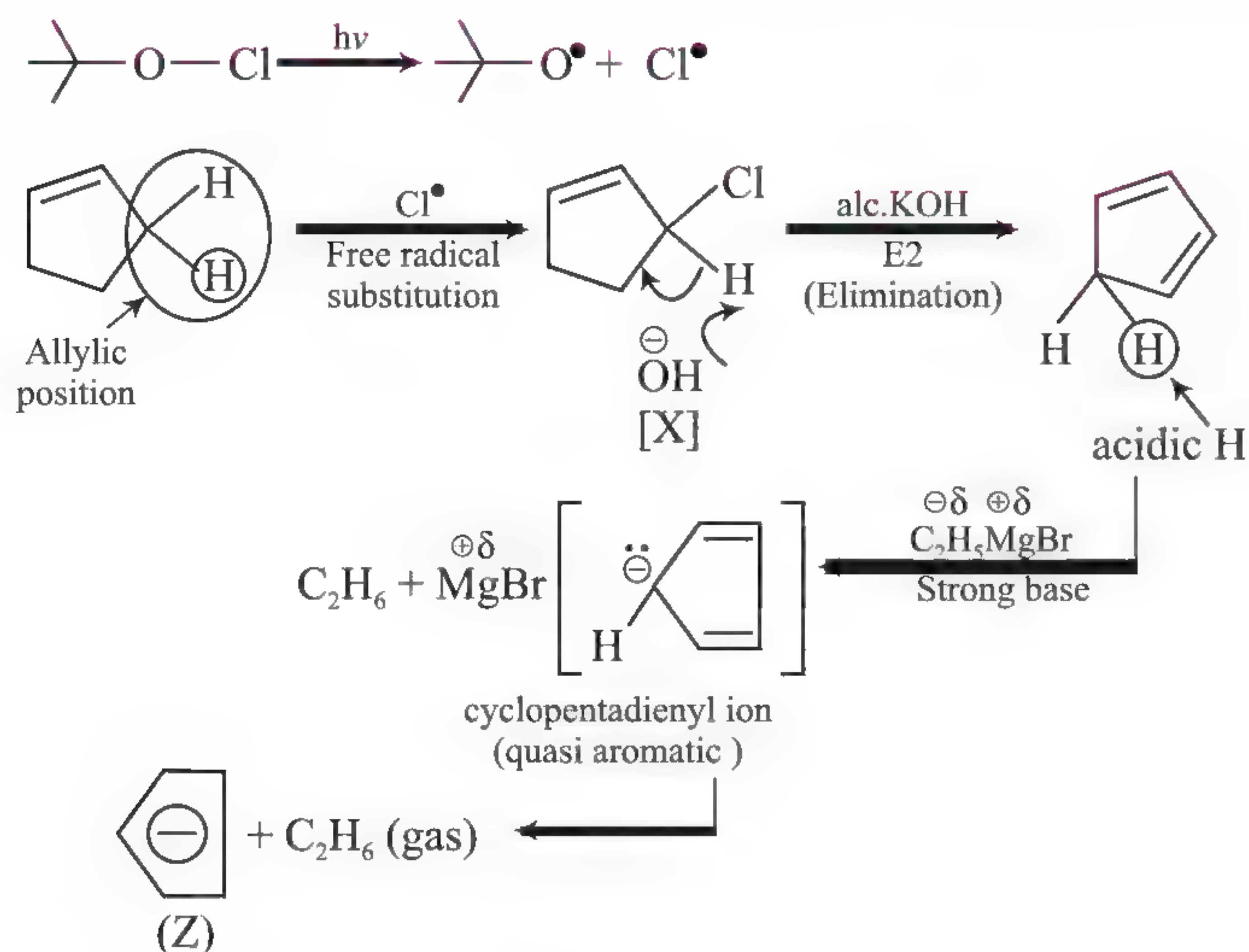
Reactivity of $\text{SN}^1 \propto$ Stability of benzyl carbocation



Stability of benzyl carbocation decreases and reactivity of SN reaction also decreases.

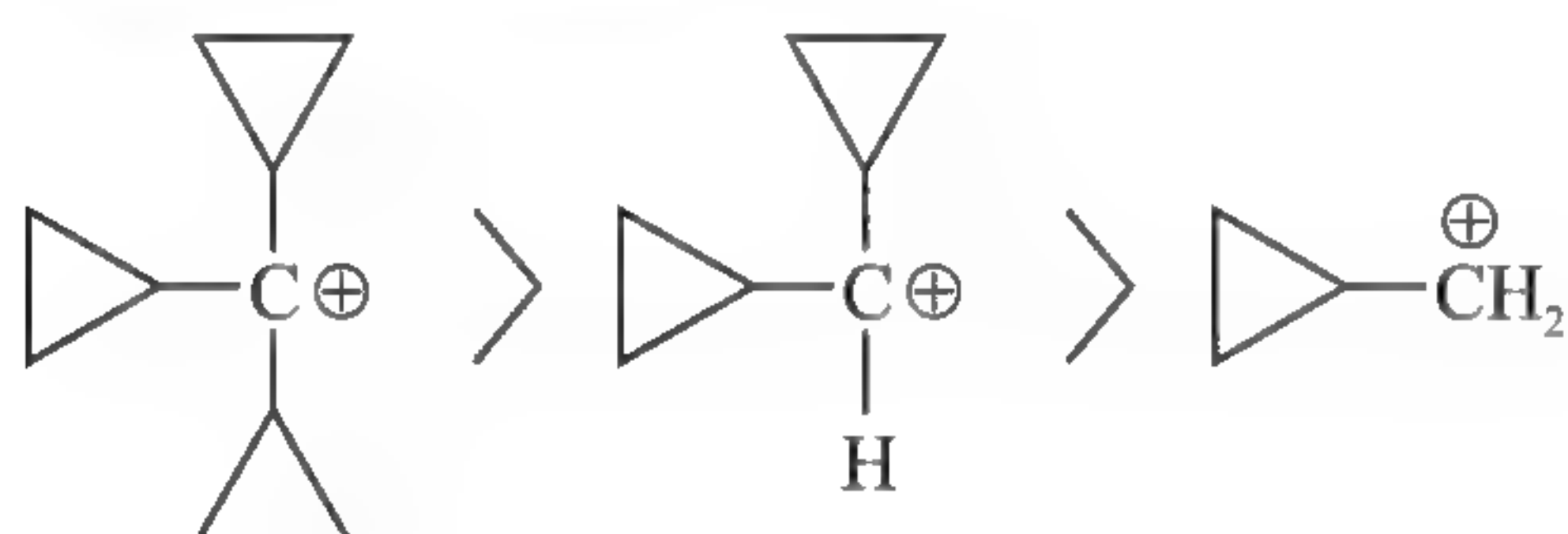
121. (4)

Both *t*-butyl hypochlorite and Cl_2SO_2 (sulfuryl chloride), with light are used for allylic chlorination by free radical substitution mechanism, e.g.,



122. (1)

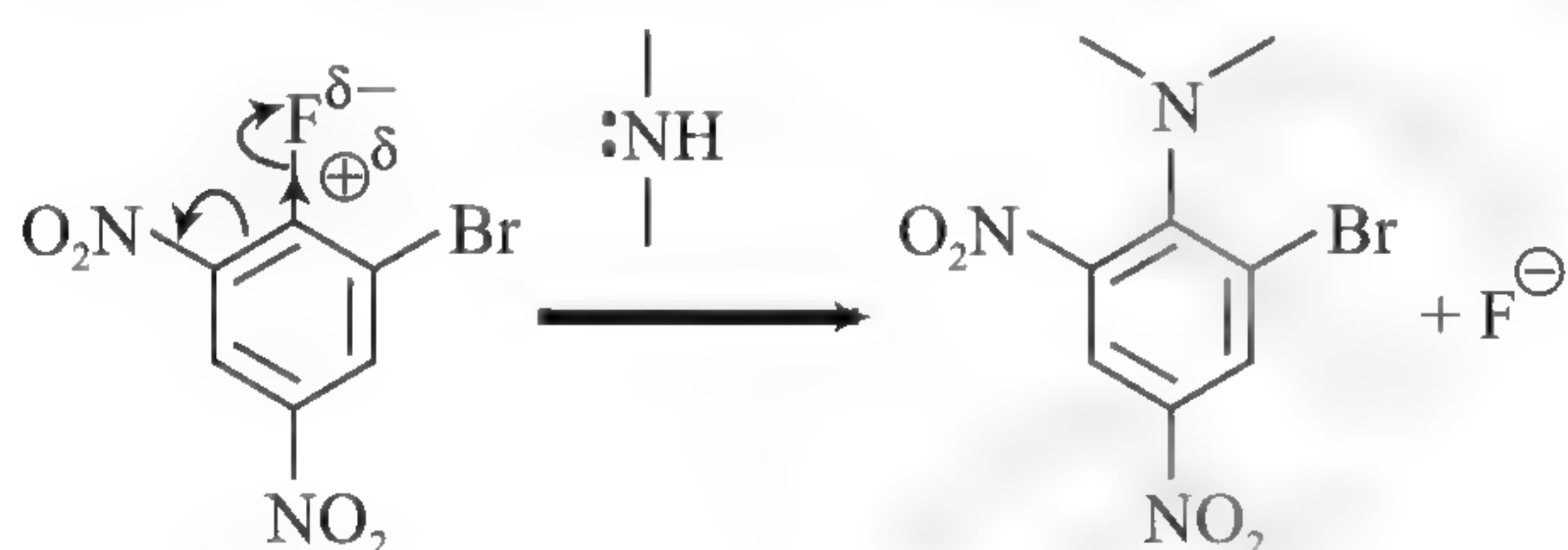
$\text{SN}^1 \text{ reactivity} \propto \text{stability of carbocation}$
 Stability of carbocation is



123. (3)

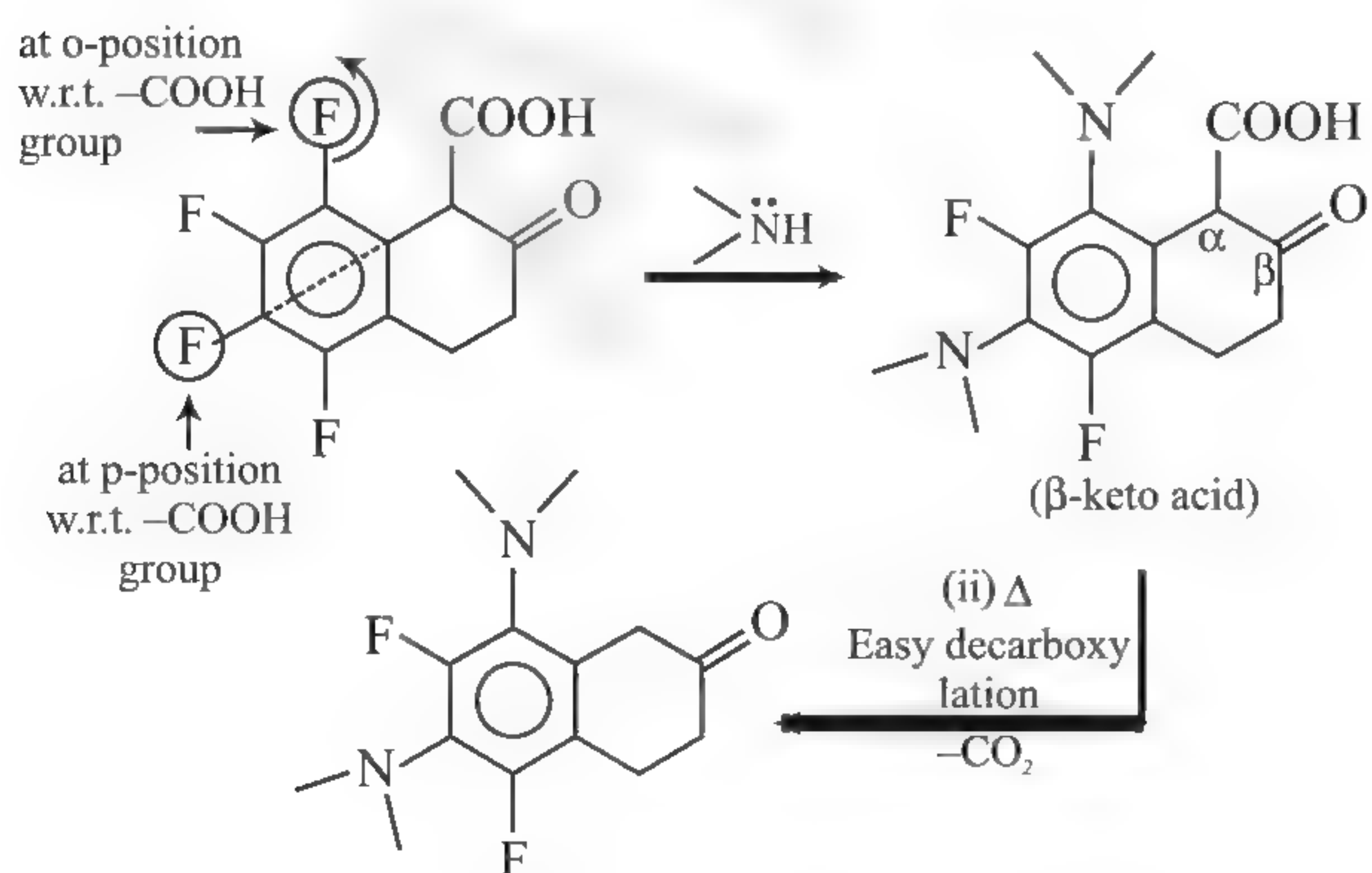
The replacement of halogens in ArX takes place under drastic conditions. The presence of EWG such as $(-\text{NO}_2)$, $(-\text{COOH})$ groups at o- and p-position (but not at m-position) w.r.t. halogen activates the halogens towards nucleophilic substitution (i.e., ArSN reaction).

Two $(-\text{NO}_2)$ groups are present at o- and p-position w.r.t. $(-\text{F})$ hence $(-\text{F})$ is displaced more easily than $(-\text{Br})$.

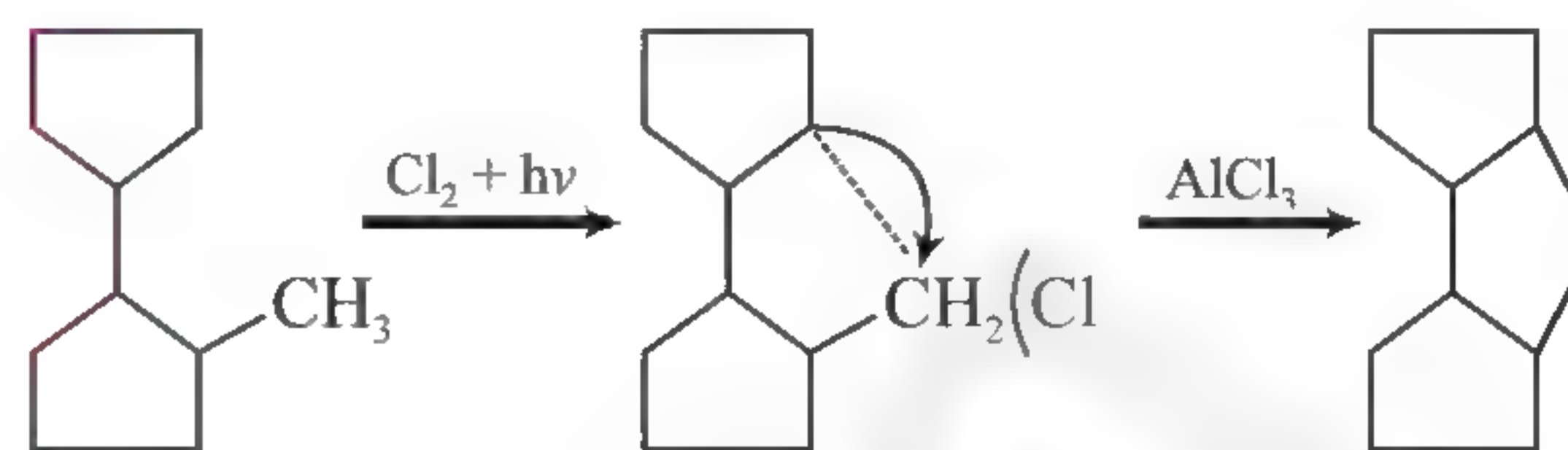


124. (2)

F^1 and F^3 are at ortho and para-position w.r.t. $(-\text{COOH})$ group and thus these two $(-\text{F})$ groups will undergo ArSN reaction with nucleophile $(>\ddot{\text{N}}\text{H})$ as shown.

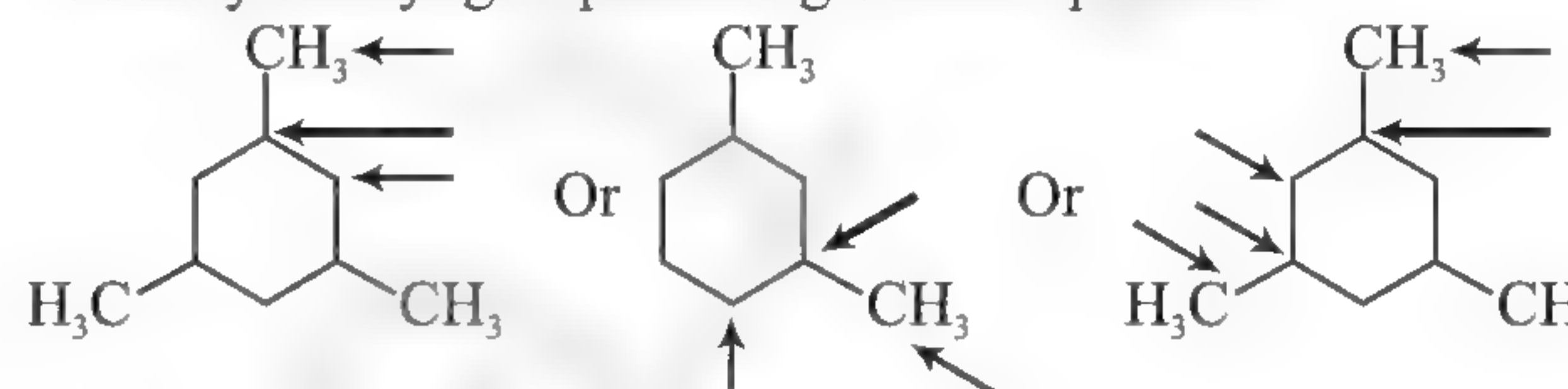
125. (1) $\text{Cl}_2 \xrightarrow{h\nu} 2\text{Cl}^\bullet$

1^{st} step converts $-\text{CH}_3$ to $-\text{CH}_2\text{Cl}$ by free radical mechanism, then with AlCl_3 , intramolecular cyclisation occurs to give final product.

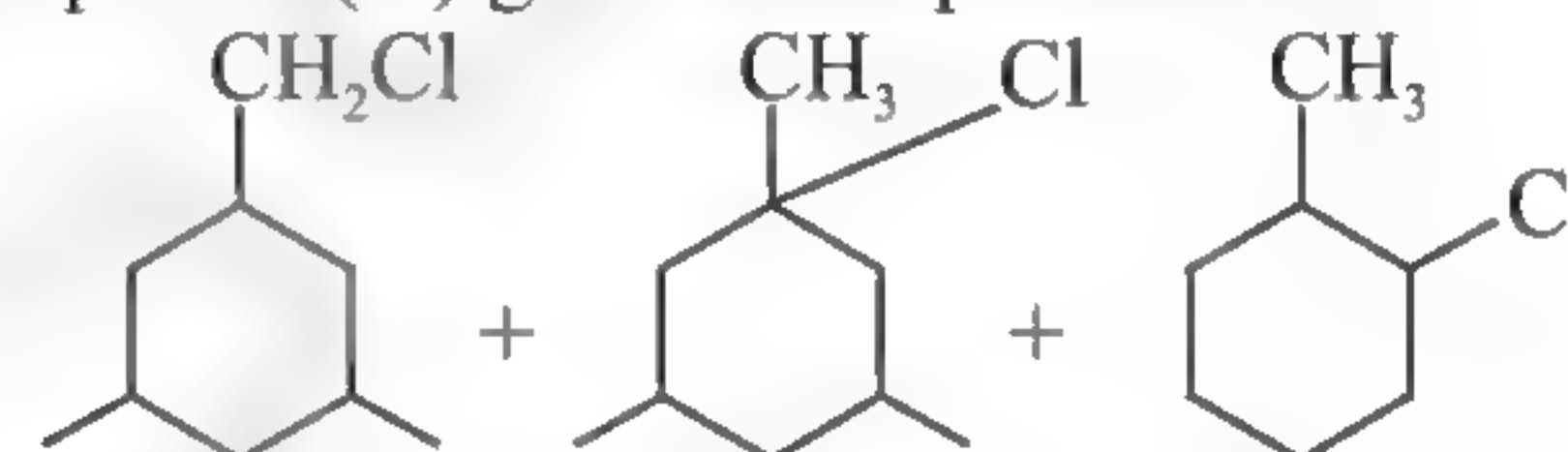


126. (3)

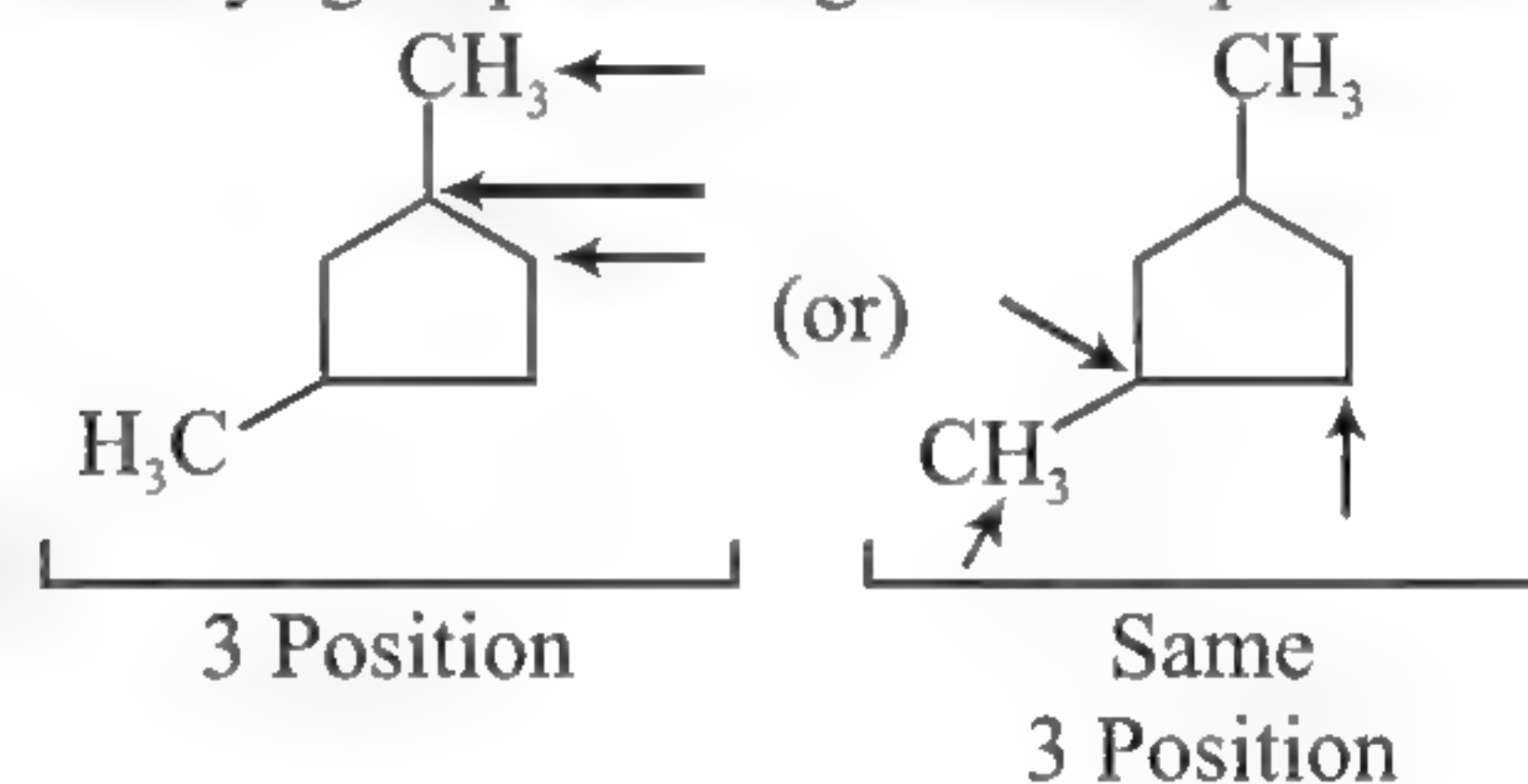
Both compounds (A) and (B) are symmetrical, monochlorination w.r.t. any methyl group would give same product.



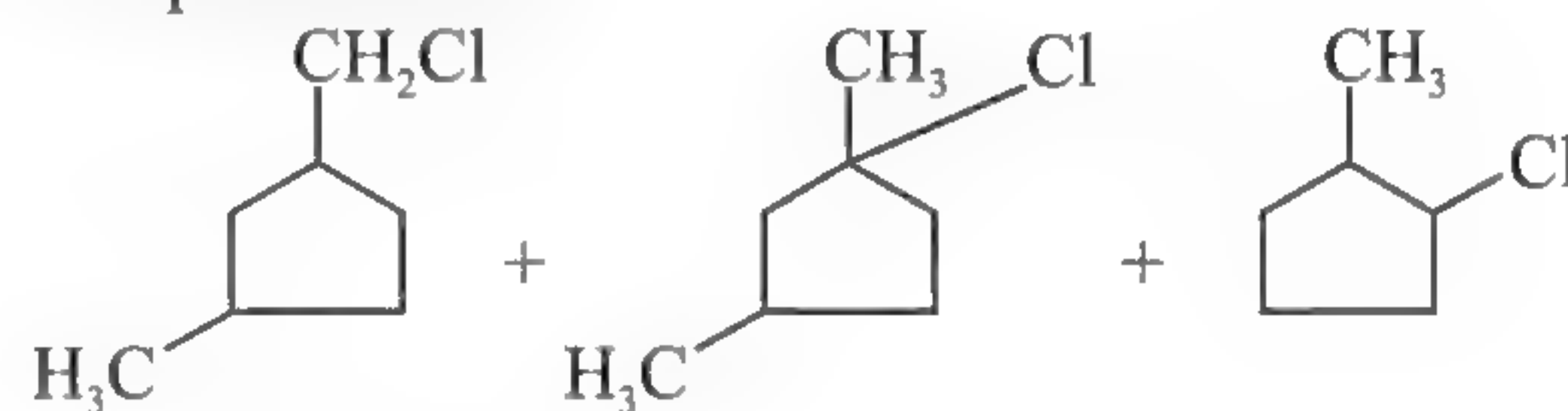
Thus compound (A) gives three products



(B) Compound (B) is also symmetrical monochlorination w.r.t. any methyl group would give same products.



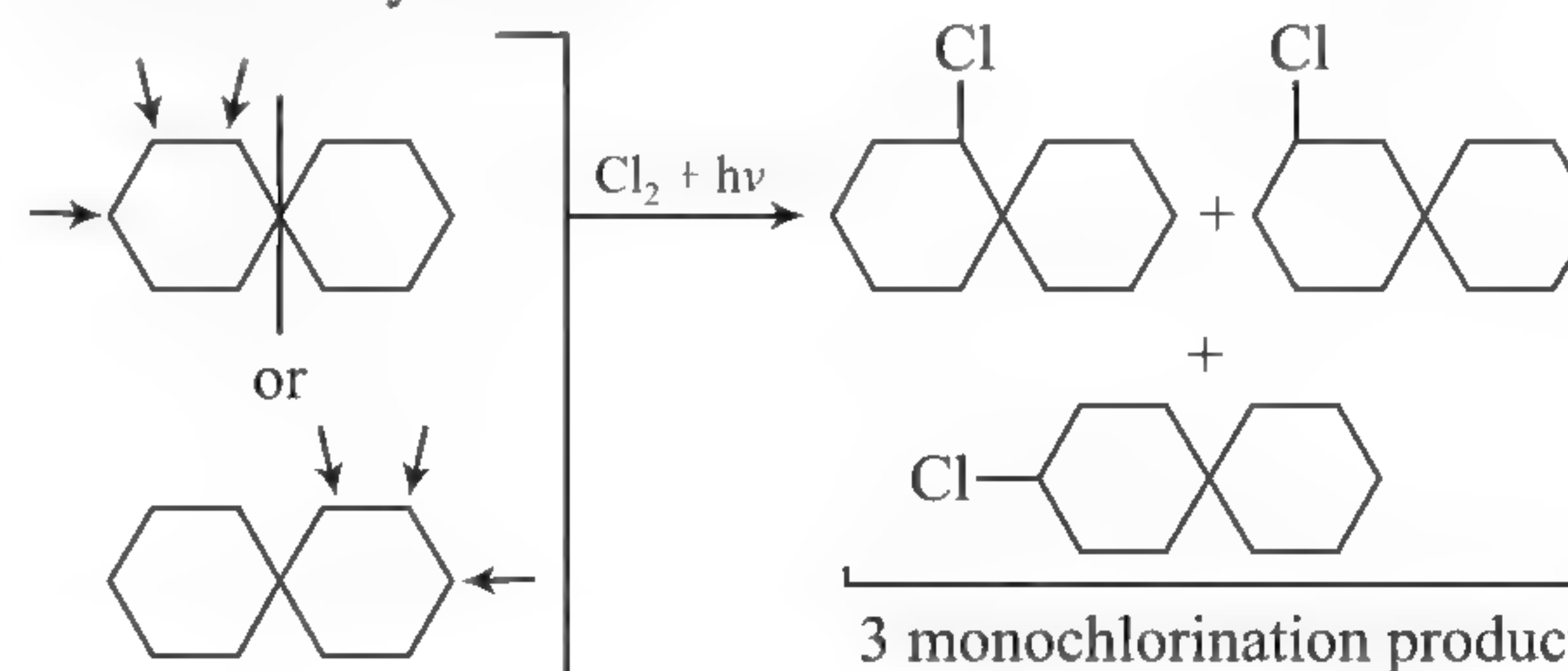
The products are:



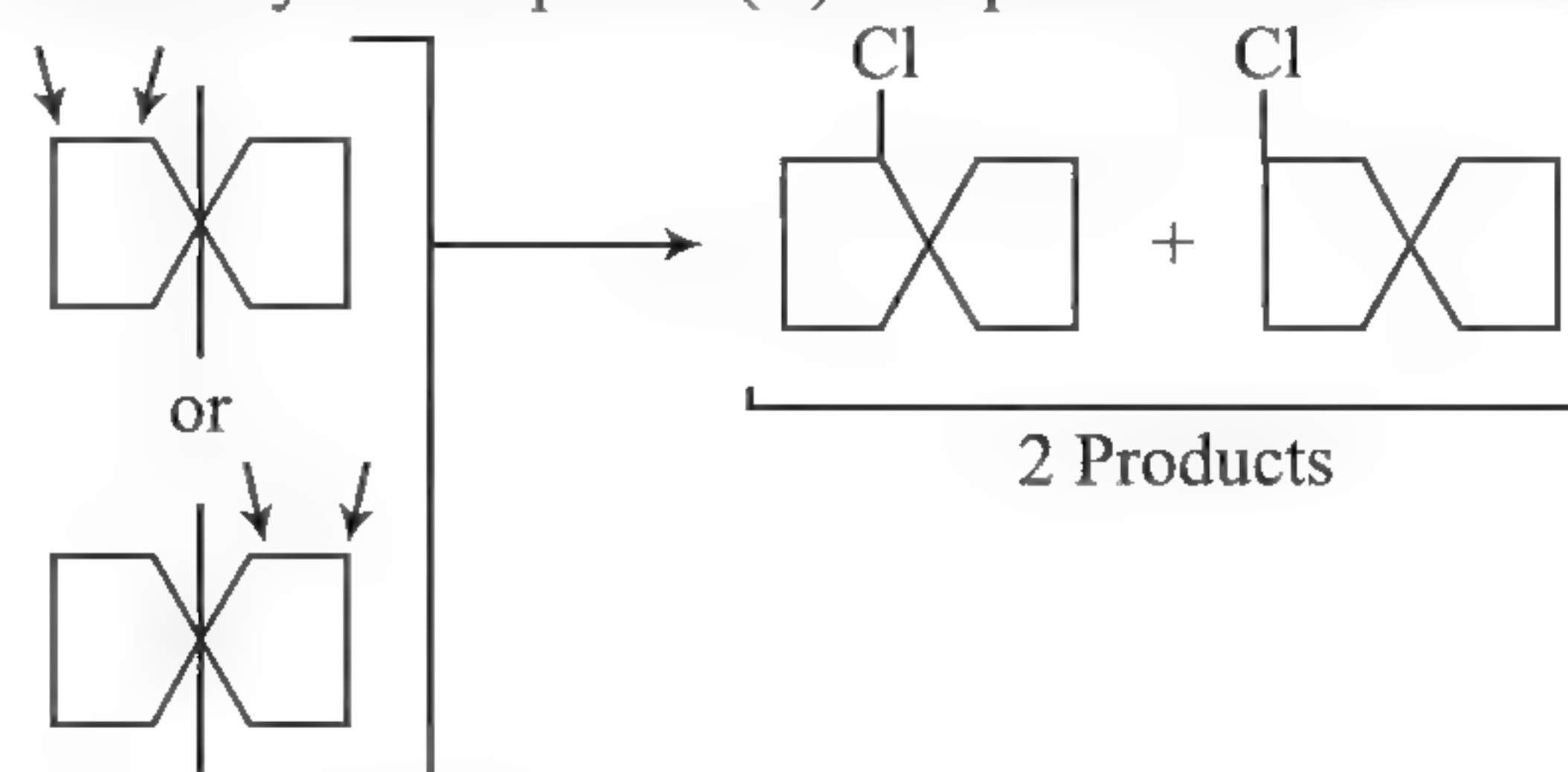
$\therefore (X) + (Y) = 6$

127. (1)

Both compounds (A) and (B) are symmetrical thus monochlorination of either ring would give same products. Position of chlorination as indicated by an arrow.



Similarly in compound (B) two products are obtained.

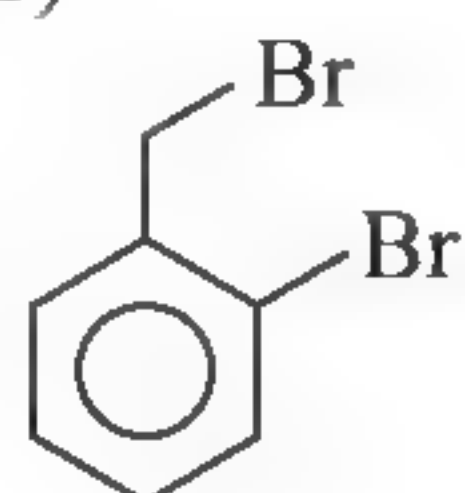


$\therefore \text{Total products} = 3 + 2 = 5$

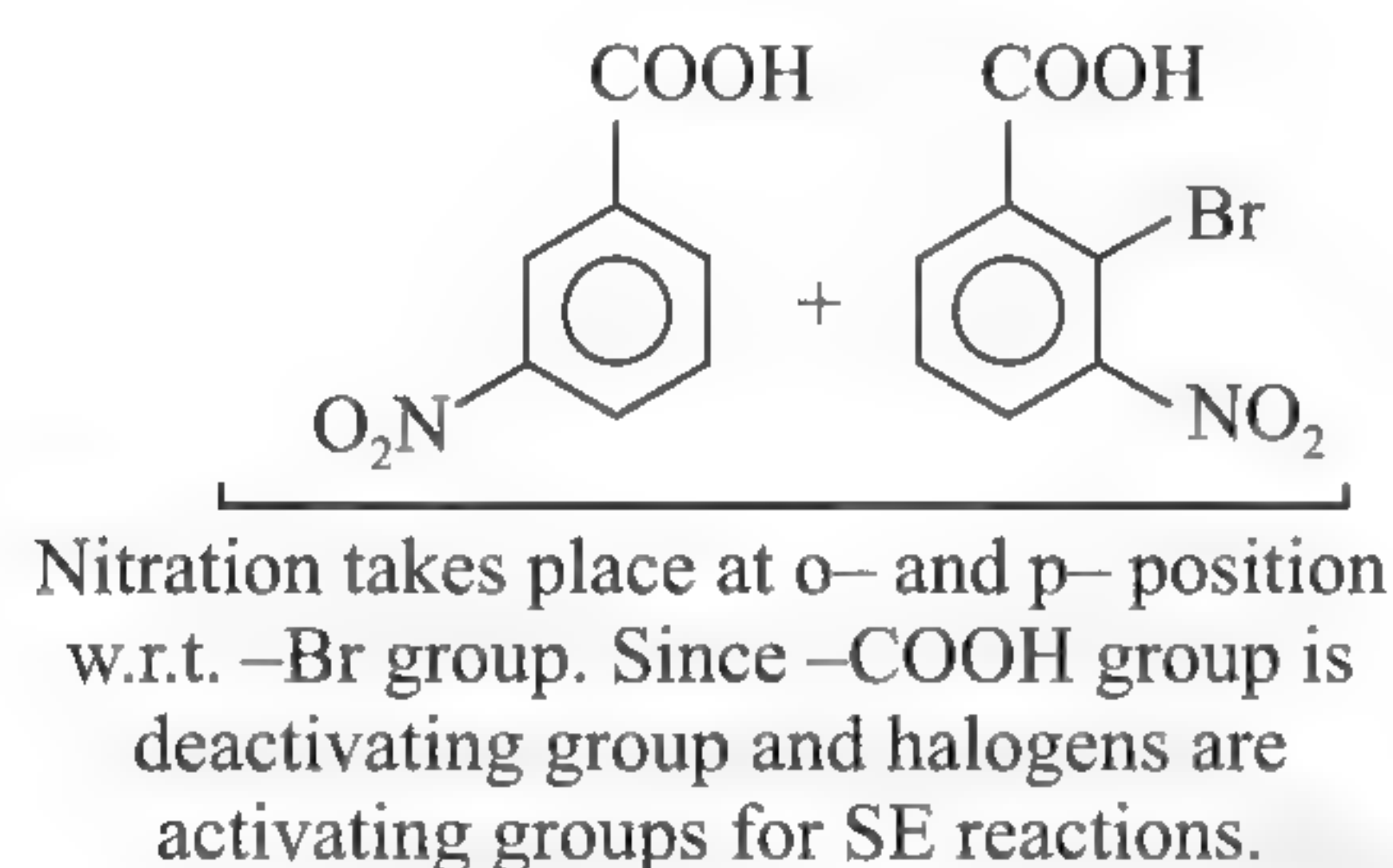
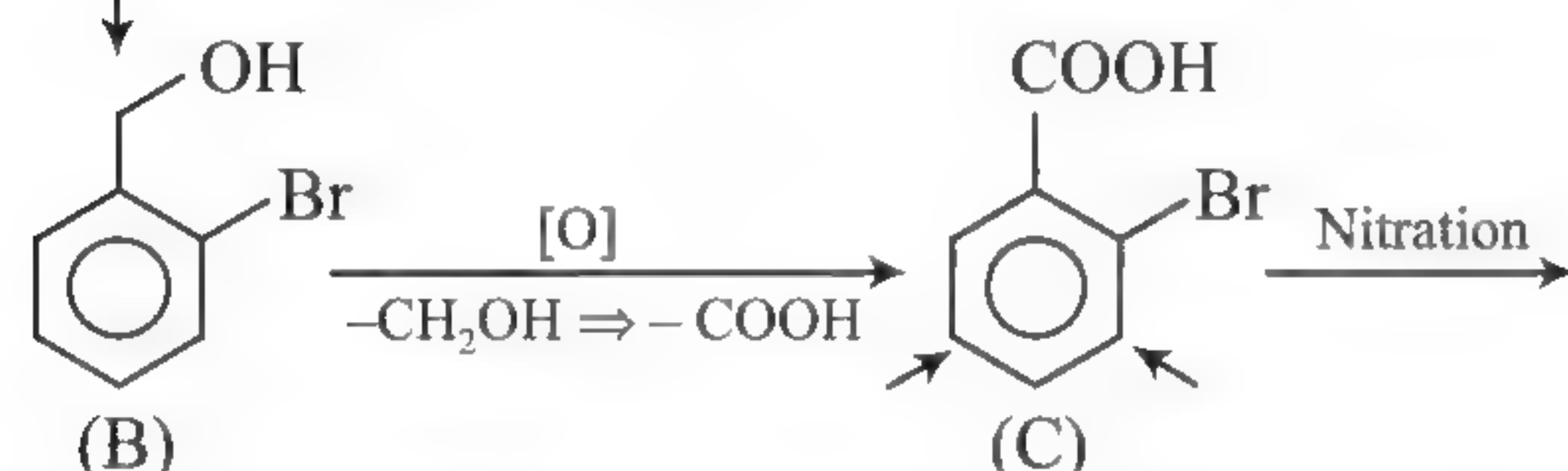
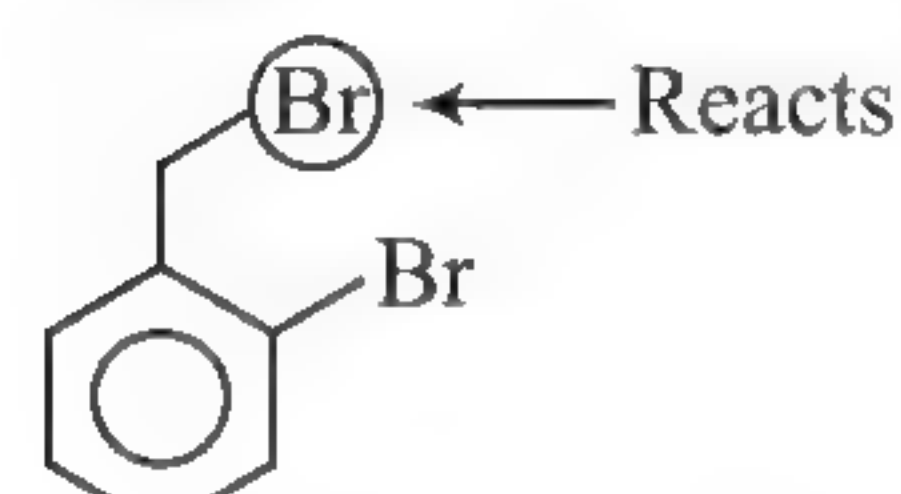
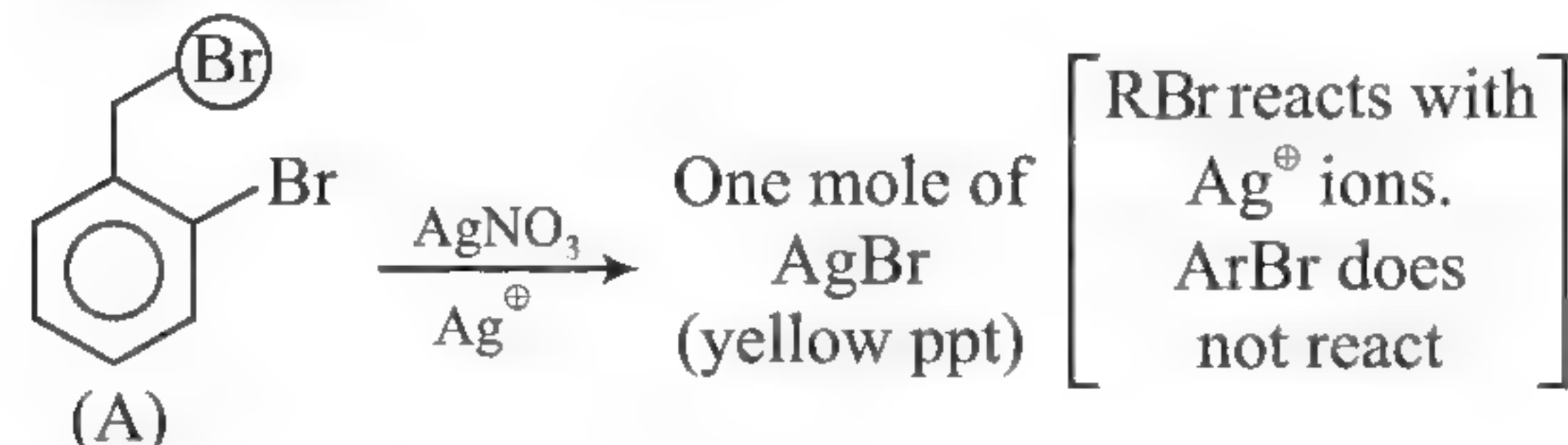
128. (3)

Formation of two mononitro derivatives from compound (C), suggests that compound (C) is an ortho-substituted product.

Rule: (OMP) (231)

Compound (A) is 

Reactions:



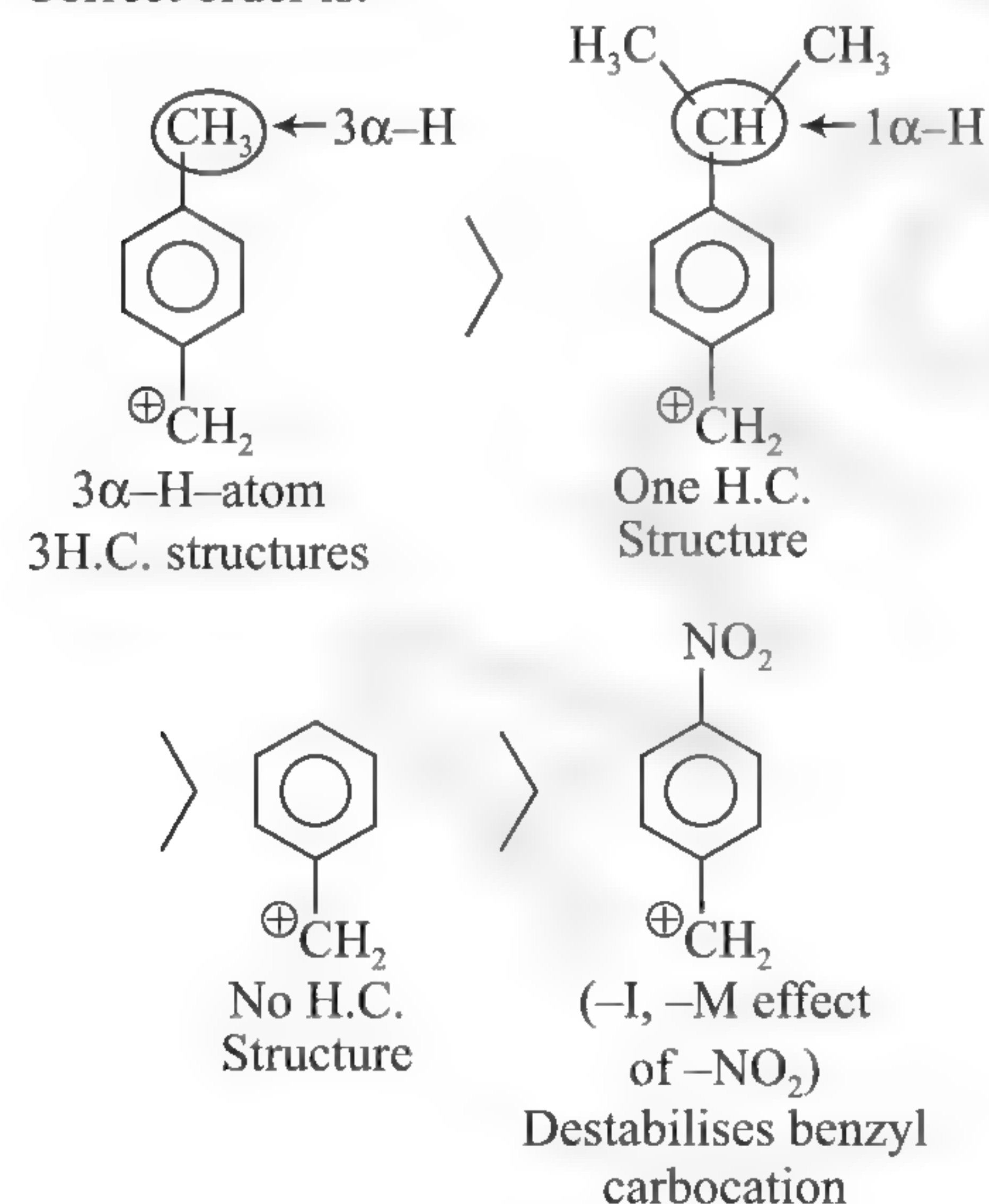
129. (2)

Reactivity of SN^1 reaction

\propto Stability of benzyl carbocation

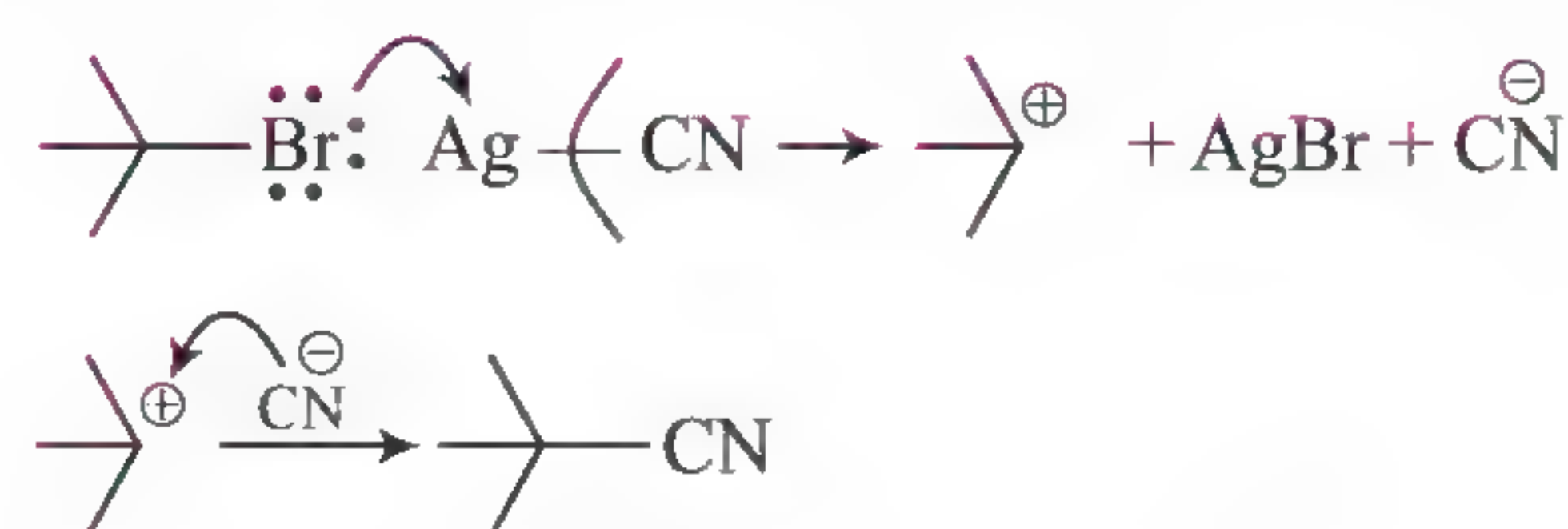
\propto EDW \propto No of H.C. structures

Correct order is:



130. (1)

With alcoholic AgCN, reaction proceed by SN^1 mechanism, due to the precipitation of AgBr.



Reactivity of $\text{SN}^1 \propto$ stability of carbocation.

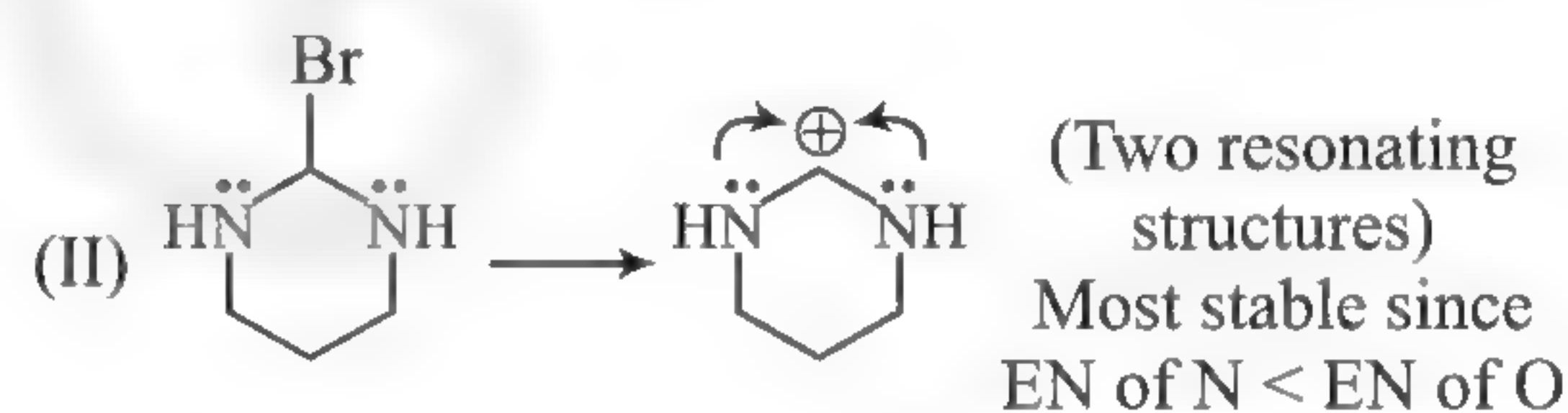
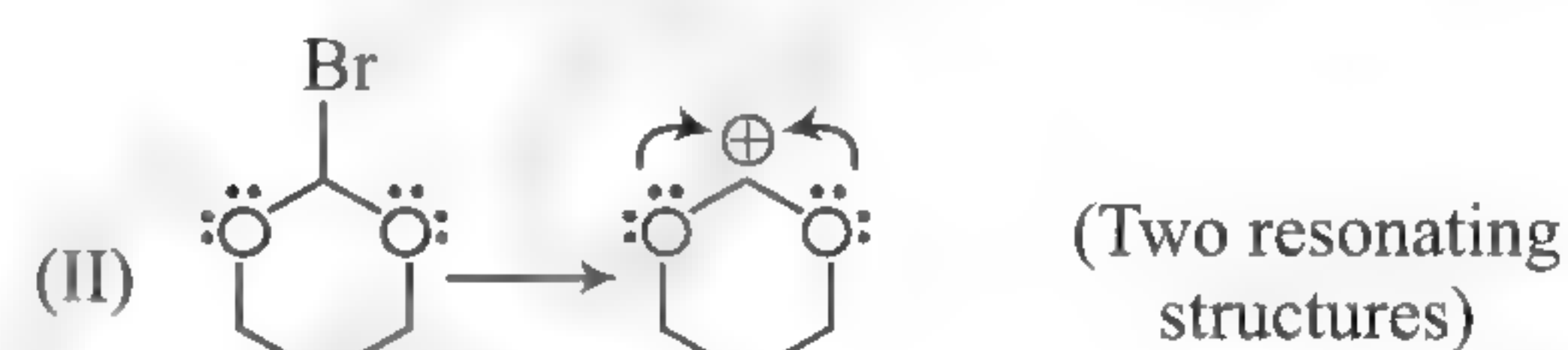
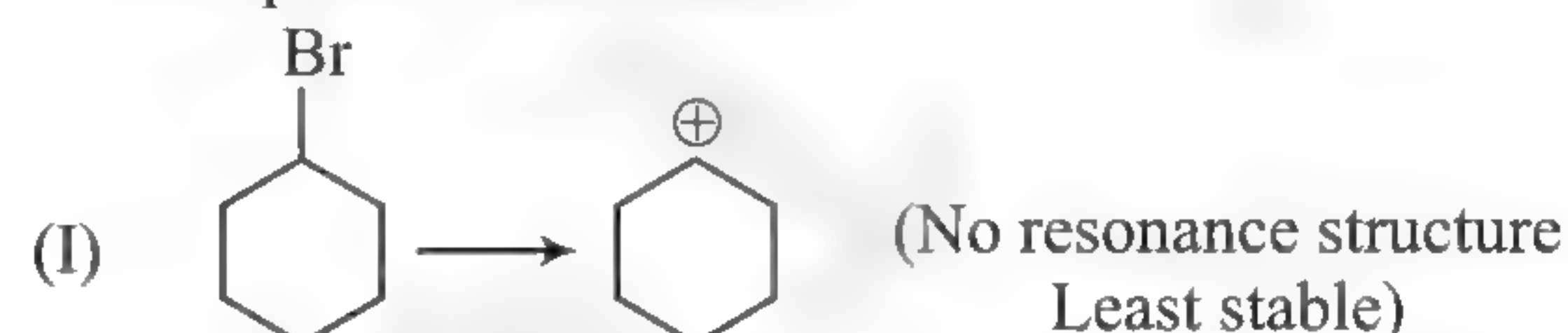
Note: With KCN, reaction proceeds via SN^2 mechanism, then answer is (1).

131. (2)

SN^1 reactivity \propto stability of carbocation

\propto More number of resonating structures

\propto Lone pair of less EN atom.

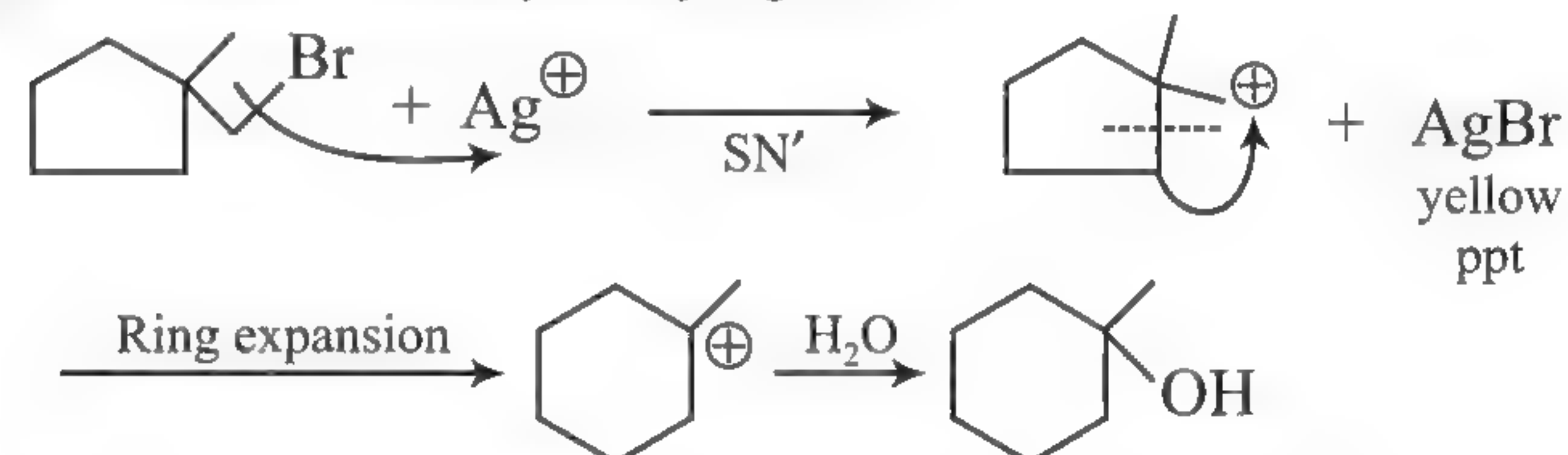


Thus SN^1 reactivity order:

III > II > I

132. (3)

SN^1 reaction is catalysed by Ag^+ ion



Note: Formation of yellow ppt. is the driving force to form 1°C^+ .

133. (1) The basic character of hydrides of 15 group decreases down the periodic table because size increases down the group and LP \bar{e} density decreases.

$\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3$.

134. (2) Since nucleophilic centre is different and belongs to the same group, so basic character and nucleophilicity are reversed.

$\text{SbH}_3 > \text{AsH}_3 > \text{PH}_3 > \text{NH}_3$.

135. (2) Weaker the base or stronger the acid, stronger is the leaving group.

$\text{SbH}_3 > \text{AsH}_3 > \text{PH}_3 > \text{NH}_3$

136. (1) Stronger the acid, weaker is its CB.

Acidic: $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$

Basic: $\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{F}^-$

137. (2) Since nucleophilic centre is different and they belong to the same group, so basic character and nucleophilicity are reversed.

$\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$

138. (2) Weaker the base or stronger the acid, stronger is the leaving group.

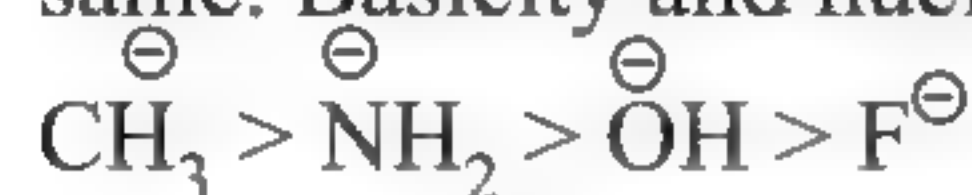
$\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$

139. (1) Stronger the acid, weaker is its CB.

Acidic: $\text{HF} > \text{H}_2\text{O} > \text{NH}_3 > \text{CH}_4$

Basic: $\text{F}^- < \text{OH}^- < \text{NH}_2^- < \text{CH}_3^-$

140. (1) Since the nucleophilic centre is different but they belong to the same period, so the basic and nucleophilic characters are same. Basicity and nucleophilicity order is:



141. (2) Weaker the base or stronger the acid, stronger is the leaving group.



142. (3) Stronger the acid, weaker the CB.

- Sulphonic acids are stronger than carboxylic acids.
- Aromatic sulphonic acids are stronger than aliphatic sulphonic acids.
- More the number of EWG, stronger is the acid.



Basic:



143. (3) Same nucleophilic centre, basicity and nucleophilicity are same.



144. (4) Nucleophilicity and leaving group are reversed.



145. (1) The basic character of hydrides of 16 group decreases down the group. Size increases down the group and LP \bar{e} density decreases.



146. (2) Basicity and nucleophilicity orders are reversed.

Have different nucleophilic centre and belong to the same group.



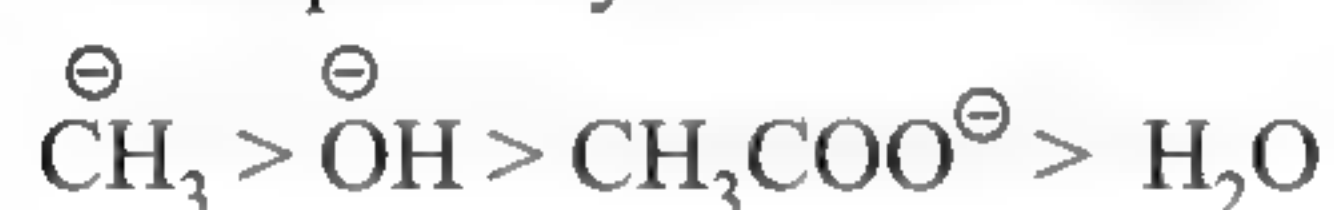
147. (2) Weaker the base, stronger is the leaving group.



148. (1) Acidic: $\text{H}_3\text{O}^+ > \text{CH}_3\text{COOH} > \text{H}_2\text{O} > \text{CH}_4$



149. (1) Compared to the others, CH_3^- has different nucleophilic centre; however, it belongs to the same period. Basicity and nucleophilicity order are same.



150. (2) Fugacity and basicity orders are reversed.



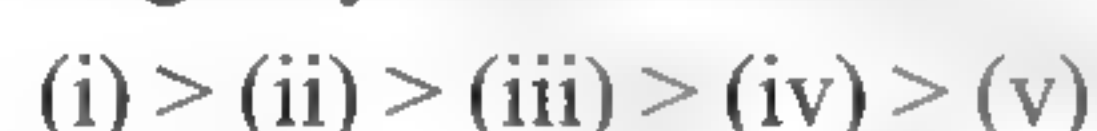
151. (1) Acidic: $\text{PhSO}_3\text{H} > \text{C}_2\text{H}_5\text{SO}_3\text{H} > \text{C}_2\text{H}_5\text{COOH} > \text{HCN} > \text{H}_2\text{O}$

Basic:



152. (1) Nucleophilic centre on CN^- is different from others, but belongs to the same period. Basic and nucleophilic orders are same. Same answer as in Q. No. 152.

153. (2) Fugacity and basic orders are reversed.



154. (3) Acidic: $\text{HCN} > \text{MeOH} > \text{H}_2\text{O} > \text{H}_2 > \text{CH}_4$



Note: MeOH is a stronger acid than H_2O , whereas other alcohols are weaker than H_2O .

155. (3) Different nucleophilic centres in $\text{CN}^- < \text{H}^- < \text{CH}_3^-$, but all belong to the same period. Basic and nucleophilic orders are same. Same answer as in Q. No. 154.

156. (4) Basicity and fugacity reversed.

Reverse answer as in Q. Nos. 154 and 155.

157. (1) More N atom and more alkyl group (+ I effect), more basic: (i) > (ii) > (iii) > (iv).

158. (1) Basic and nucleophilic orders are same.

Same answer as in Q. No. 157.

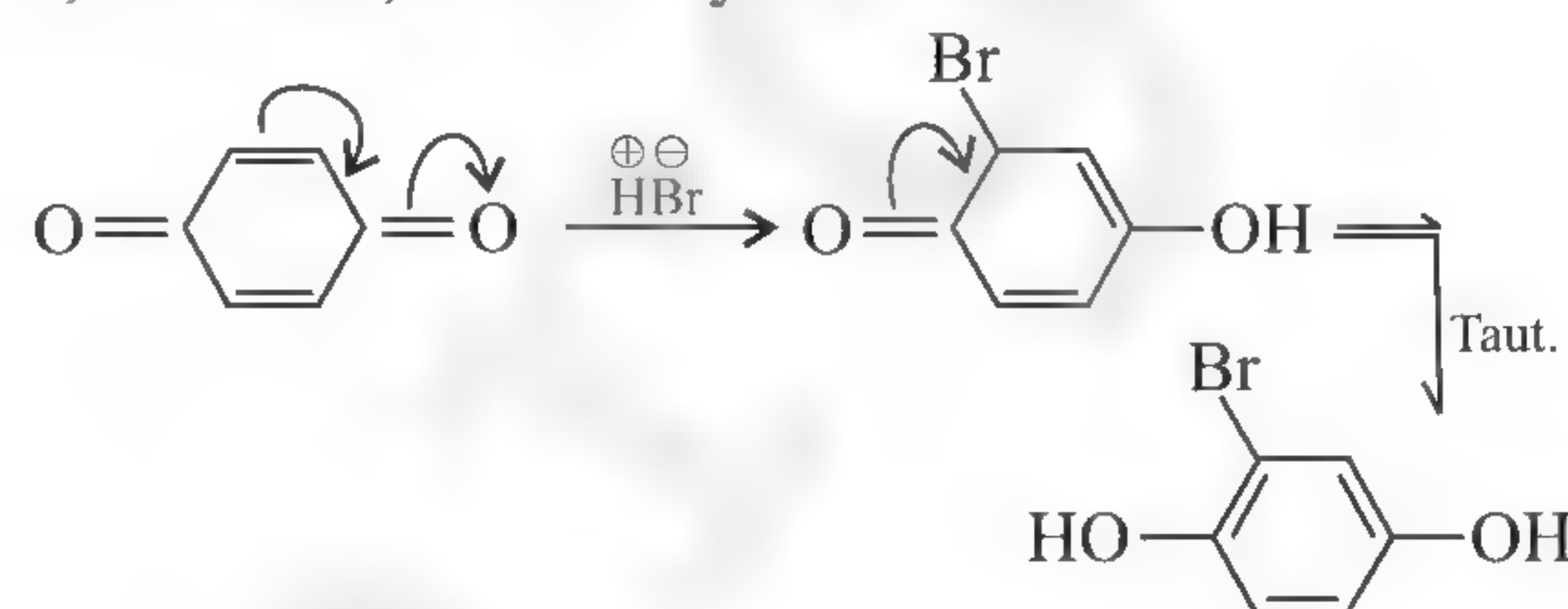
159. (2) Basicity and fugacity are reversed.

Reverse answer of Q. No. 158.

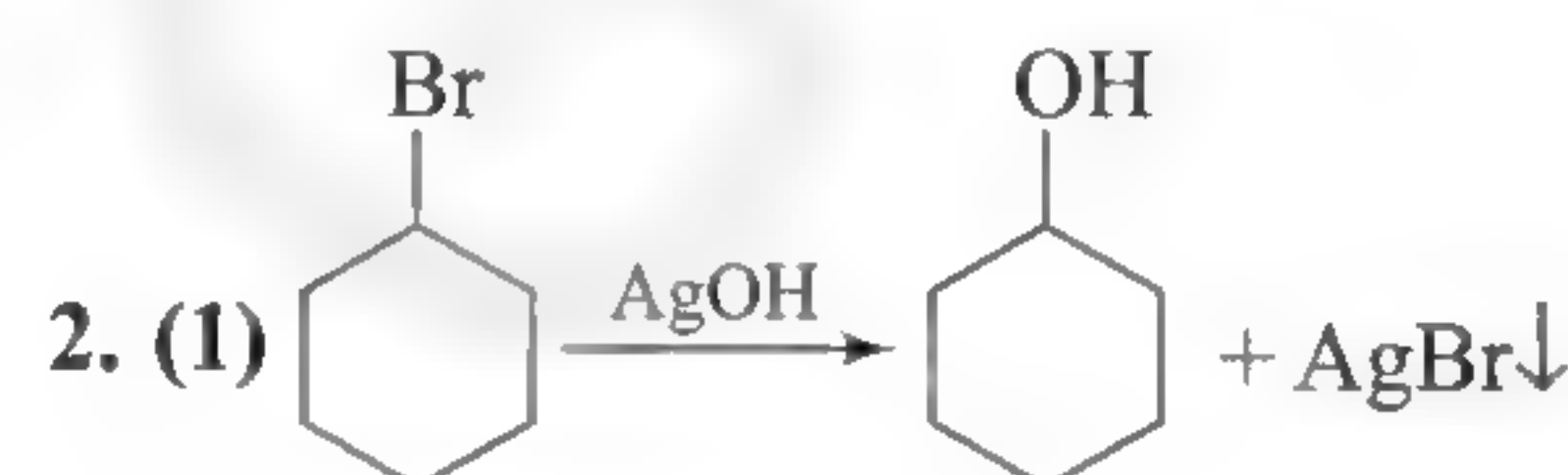
160. (2)

161. (4) Refer to Section 3.17.

162. (3) 1,4-Addition, followed by tautomerism.



Multiple Correct Answers Type

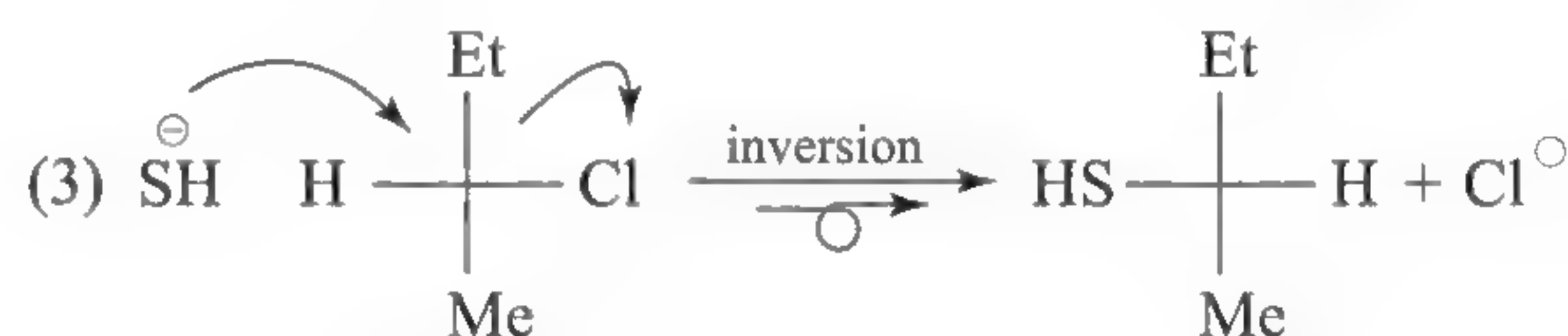
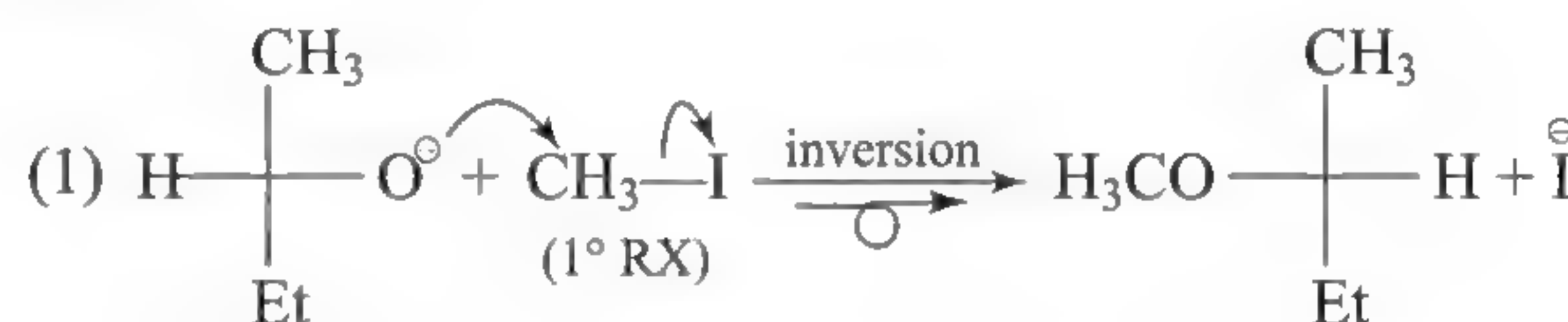


3. (1, 3, 4)

Mechanism of $\text{S}_\text{N}1$ and $\text{E}1$ is controlled by stability of carbocation.

Mechanism of $\text{E}2$ is decided by no. of α -H in alkane

4. (1, 3)

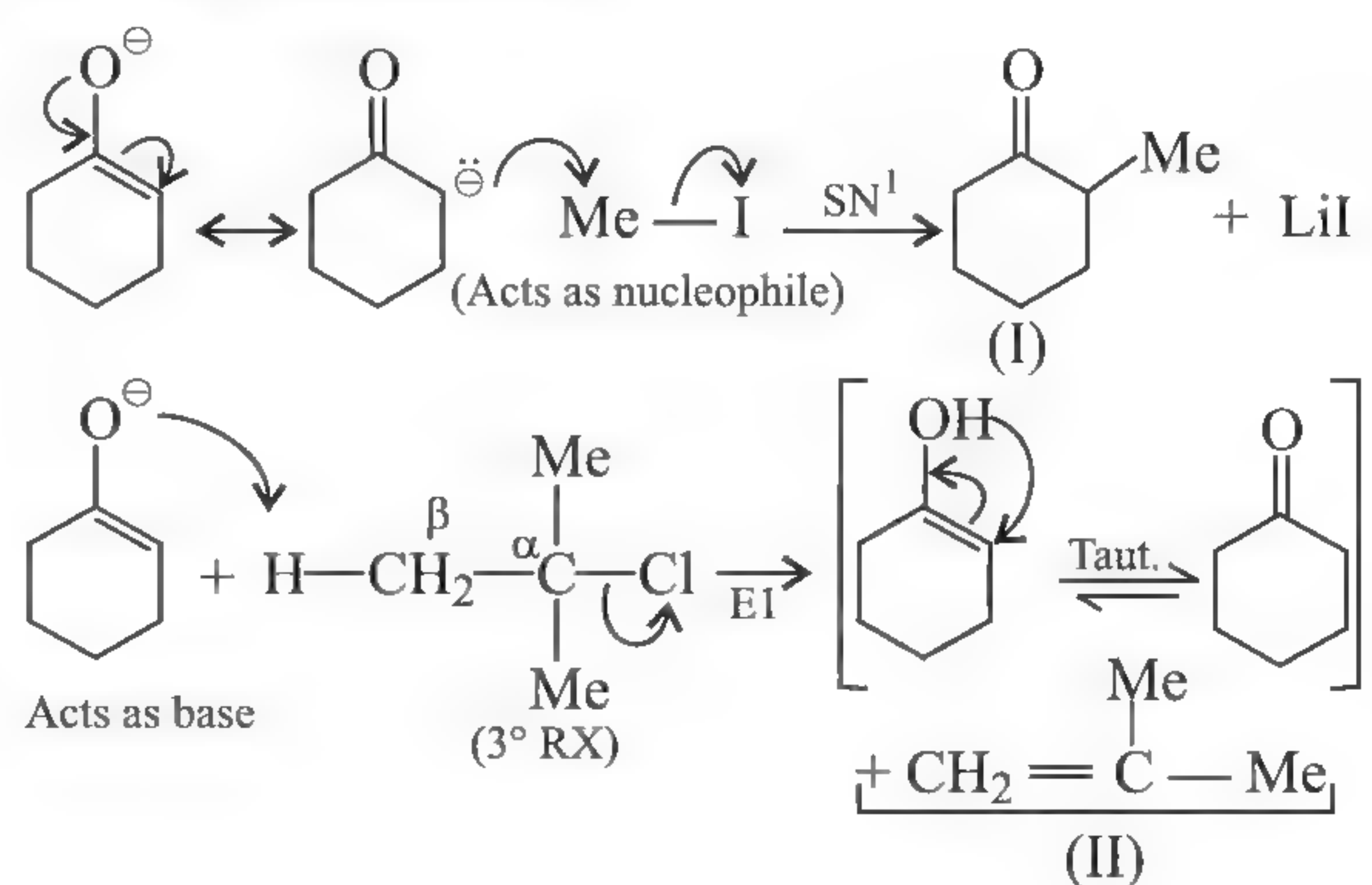


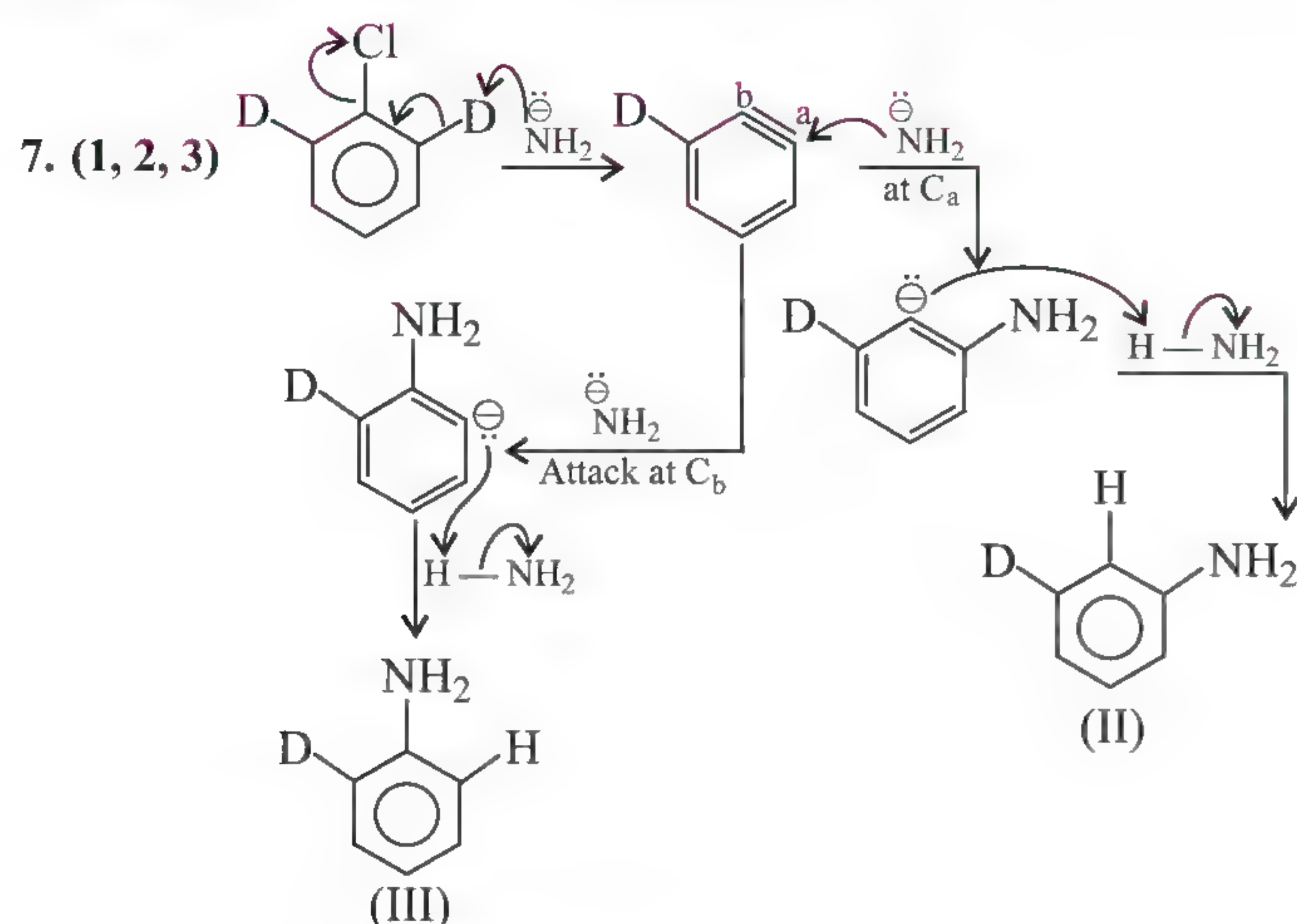
5. (1, 2, 3)

For explanation, see Section 3.10.

6. (1, 2)

The lithium enolate bases from cyclohexanone react with alkyl halides in different ways.



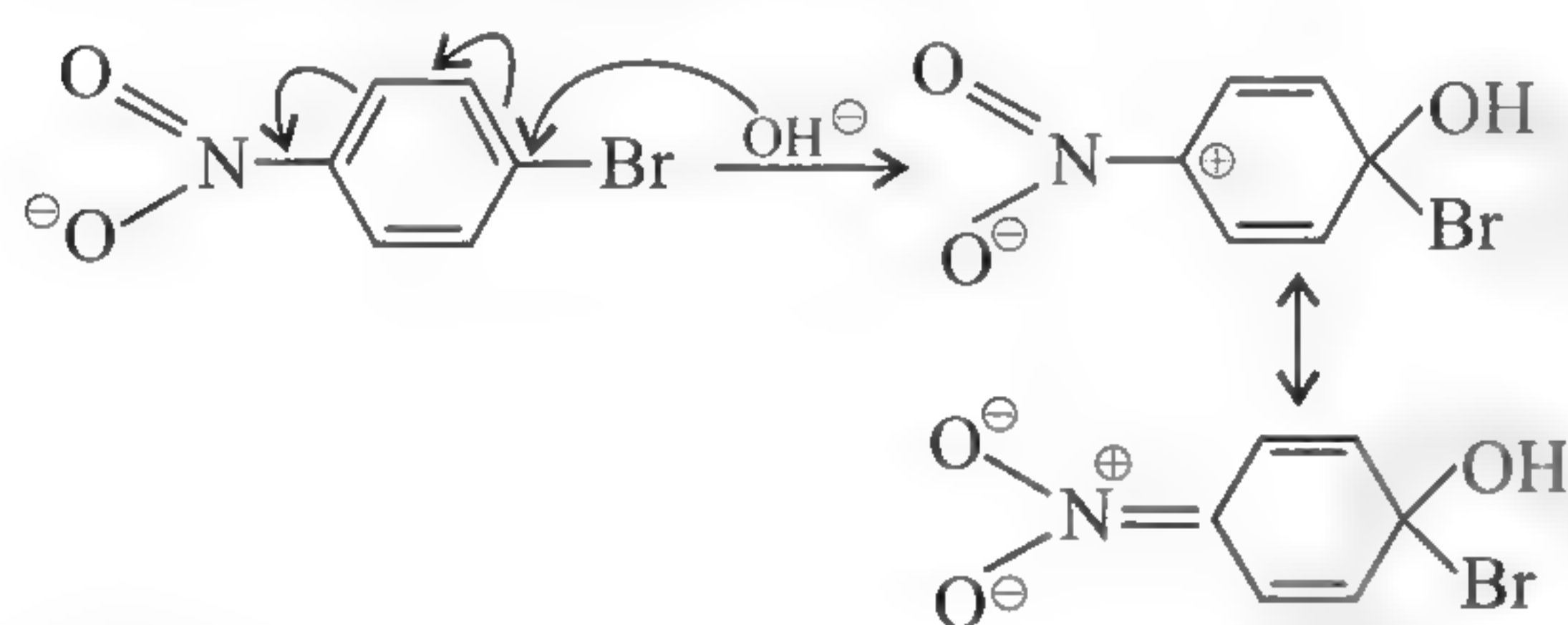


Product (II) is cine substitution and product (III) is direct substitution. Reaction is ArSN (elimination–addition) reaction.

8. (1, 2, 3)

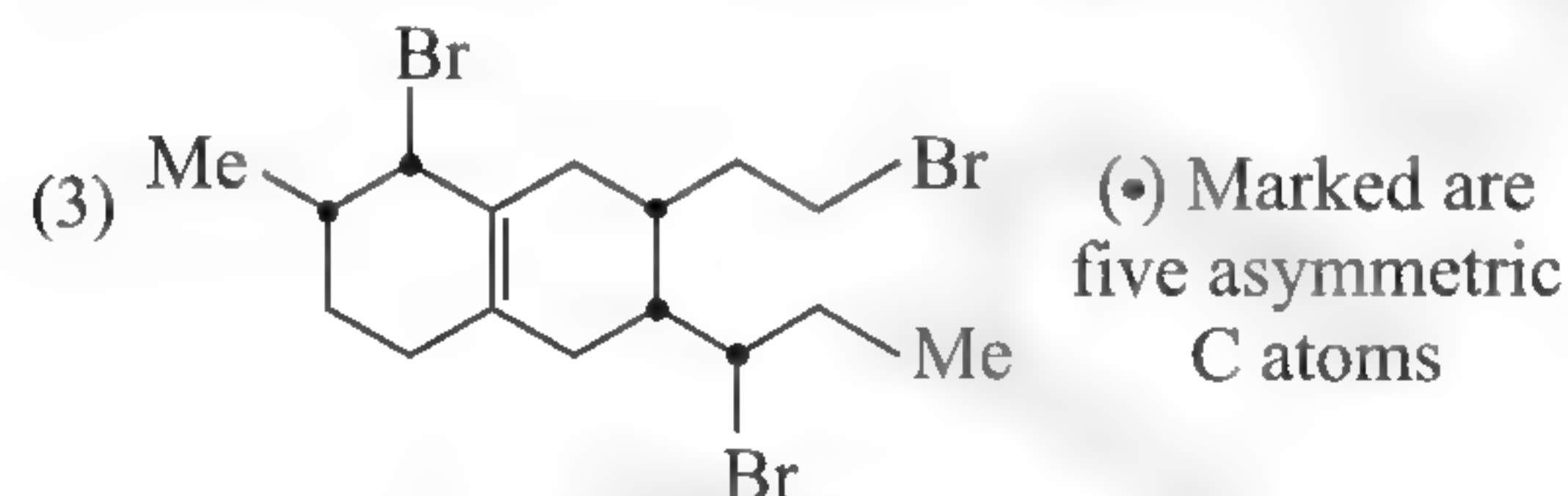
- (1) SE reaction by $(\text{NO}_2)^+$, species (I) is not formed. So (1) is a correct statement.
- (2) SE reaction by Br^+ , $(-\text{NO}_2)$ is *m*-directing, Br^+ will attack at *m*-position. Species (I) is not formed. So (2) is a correct statement.
- (3) SE reaction by Br^+ , $(-\text{OH})$ group is *o*- and *p*-directing (class — OH decides orientation), *p*-position is blocked. Species (I) is not formed. So (3) is a correct statement.

- (4) ArSN reaction (addition–elimination) reaction by OH^- nucleophile. Species (I) is formed. So (4) is an incorrect statement.



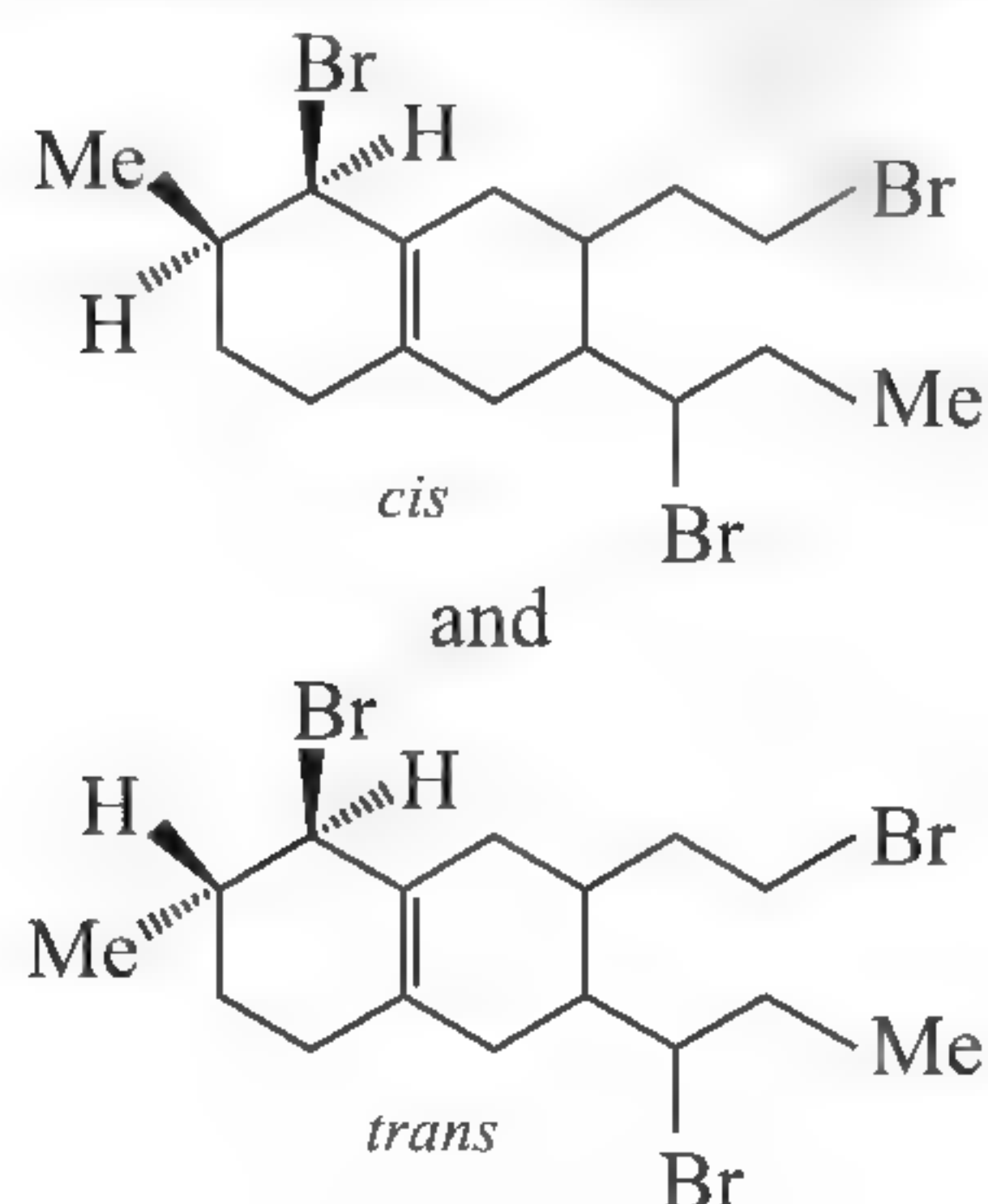
9. (1, 2, 3)

- (1) Loss of Br (1) would give less-substituted alkene (more reactive, less stable).
- (2) Removal of Br (3) would give more stable 2° allylic C^+ .



Statements (1), (2), and (3) are correct.

- (4) Statement (4) is wrong, since the compound shows G.I.



10. (1, 2, 3)

Product (4) is wrong, Br_2 in non-polar solvent and gives *o*- and *p*-products.

11. (1, 2, 3)

Statements are self-explanatory.

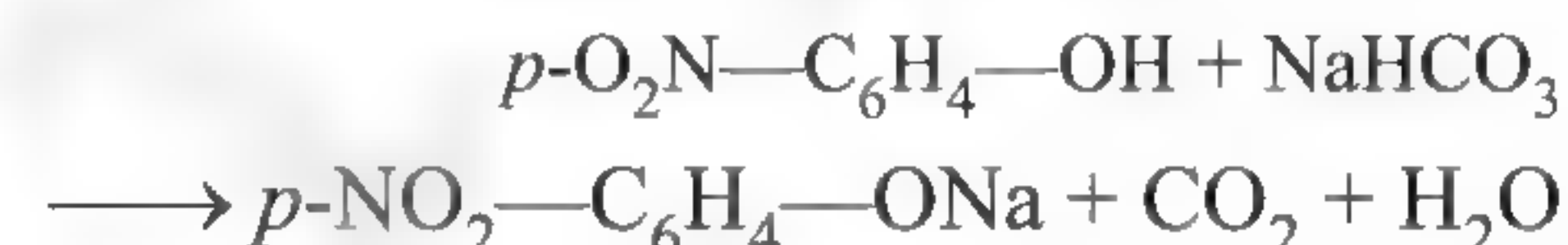
12. (1, 4)

See ipso substitution in Section 3.15.

13. (1, 2, 3)

Statements (1), (2), and (3) are correct but (4) is wrong because reaction (4) gives benzene.

14. (4) $\text{PhSO}_3\text{H} + \text{NaHCO}_3 \longrightarrow \text{PhSO}_3\text{Na} + \text{CO}_2 + \text{H}_2\text{O}$

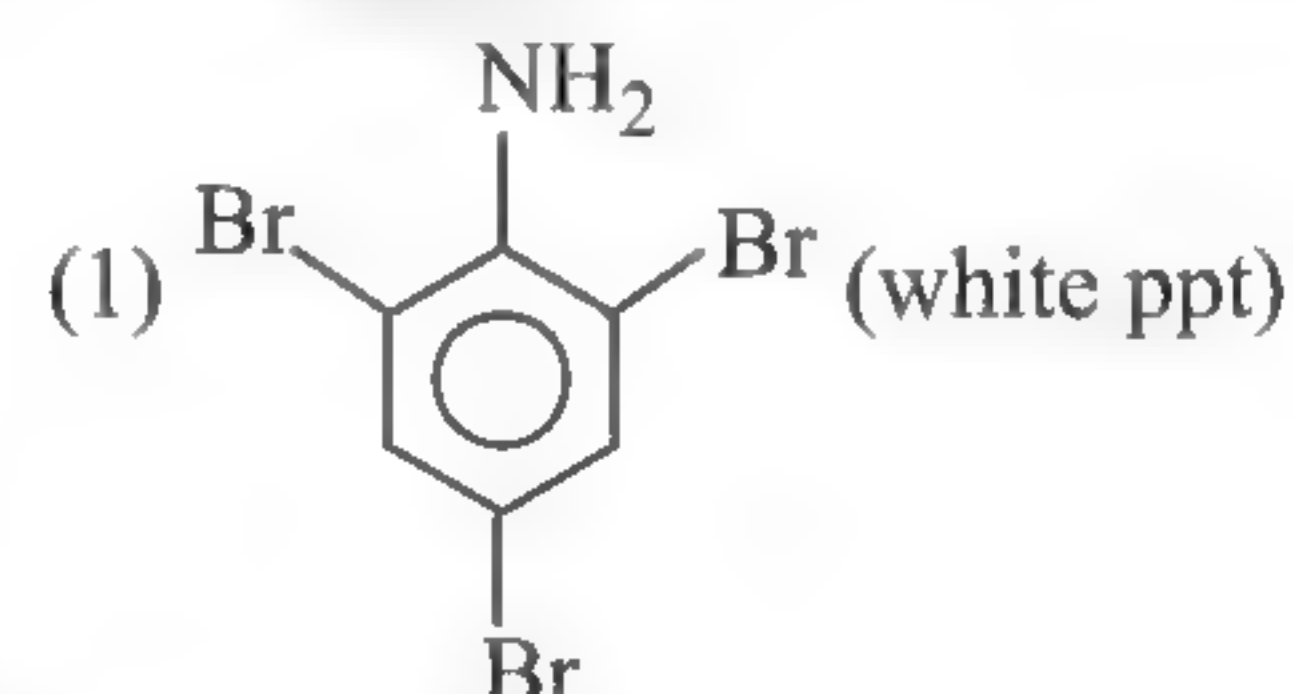


15. (1, 3, 4)

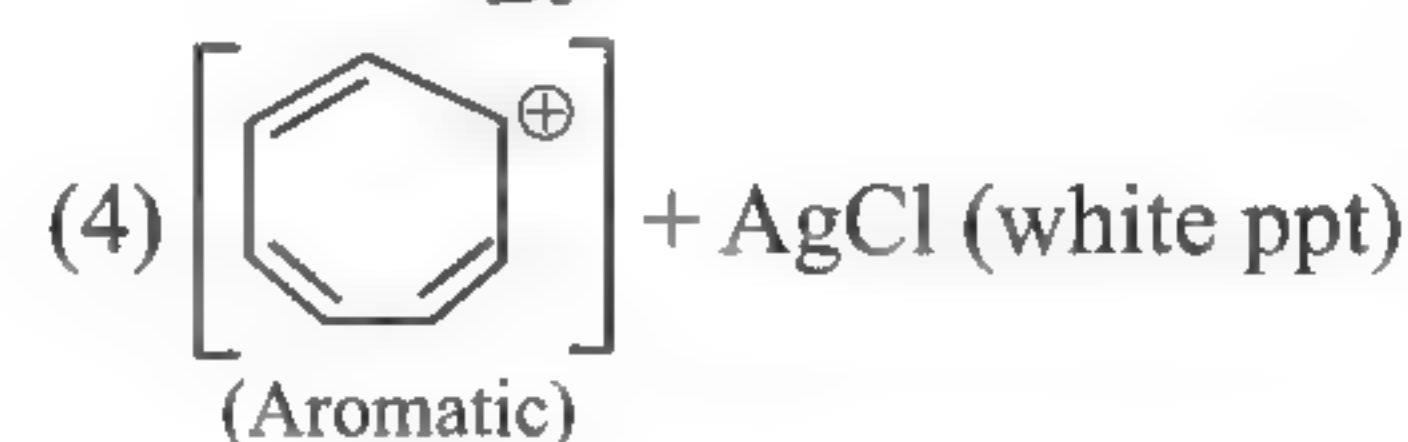
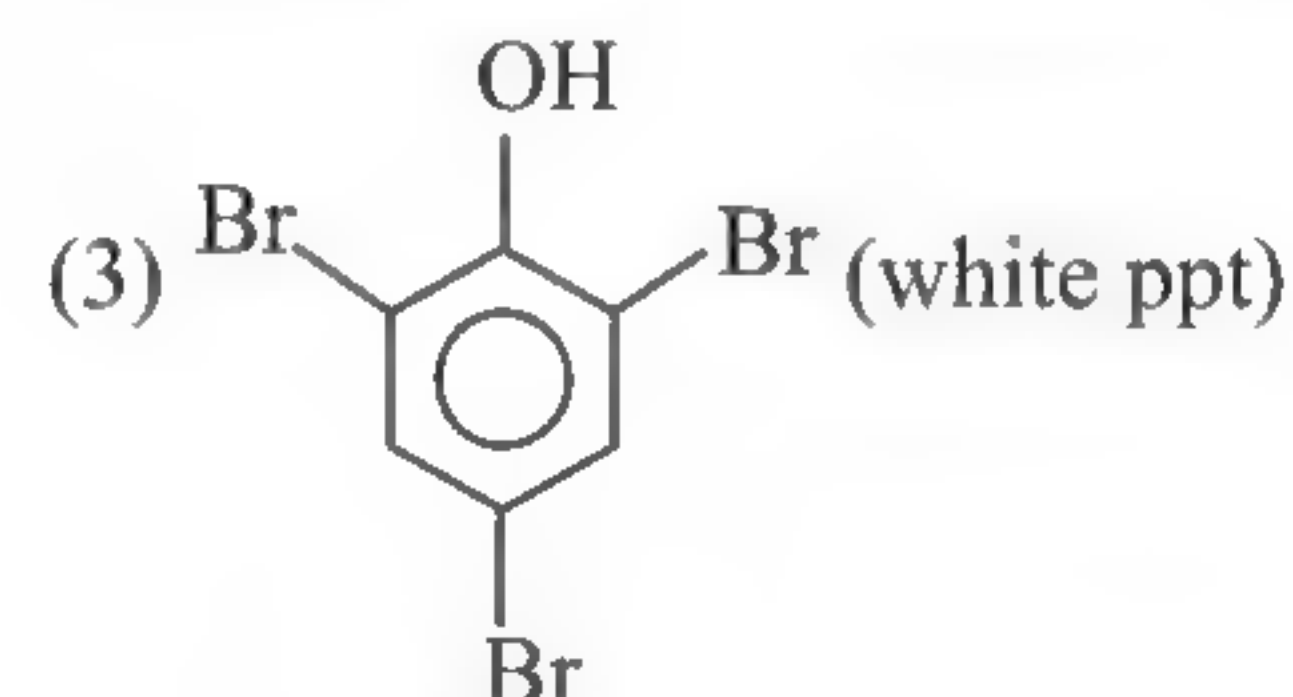
Aromatic compounds having strong electron withdrawing at *ortho* and *para* with respect to leaving group (i.e., Cl) give nucleophilic aromatic substitution reaction.

16. (1, 2, 3, 4)

It is an example of Ipso substitution.



(2) $\text{CH}_3\text{C}\equiv\text{C}-\text{Ag}$ (white ppt)



17. (1, 2, 3)

Refer to section 3.21.

Correct (1): $\text{C}_2\text{F}_3\text{Cl}_3$.

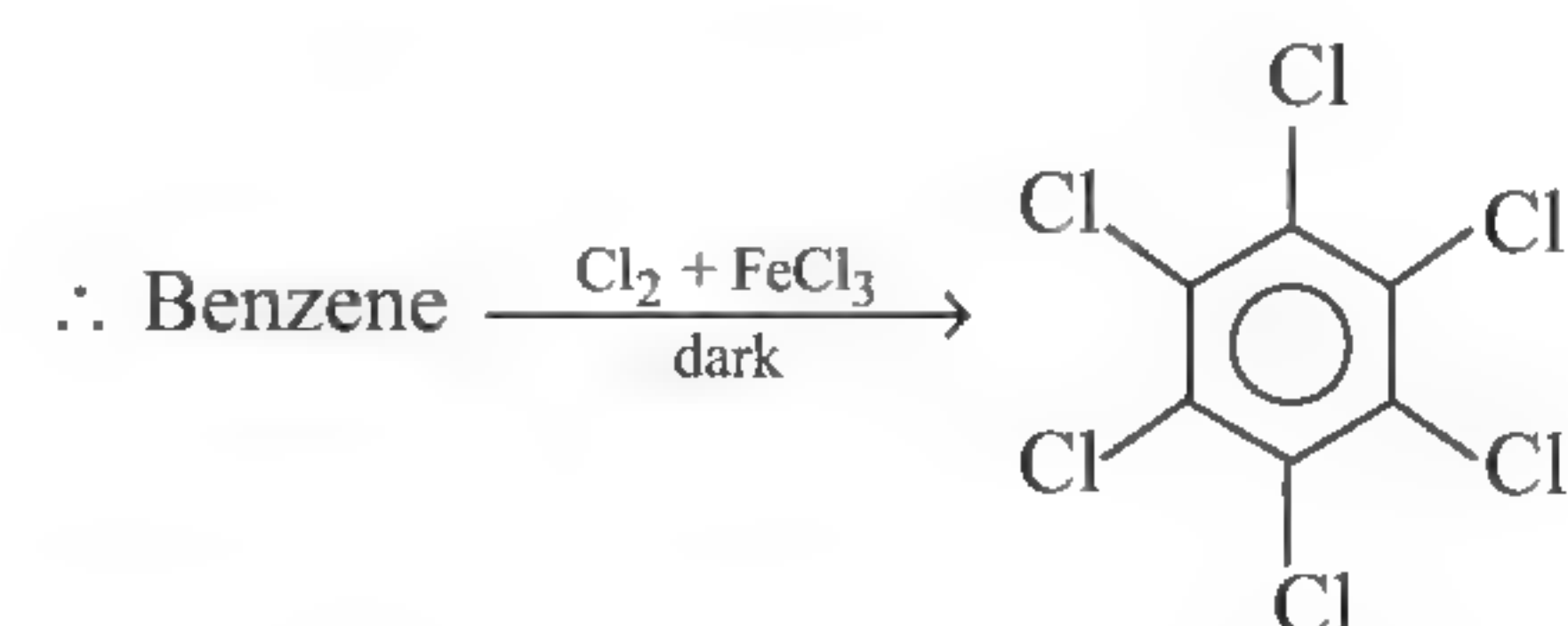
Correct (2): Two types, Freon 1210 and Freon 1111

Correct (3): $3\text{CCl}_4 + 2\text{SbF}_3 \longrightarrow 3\text{CF}_2\text{Cl}_2 + 2\text{SbCl}_3$ (Freon 12)

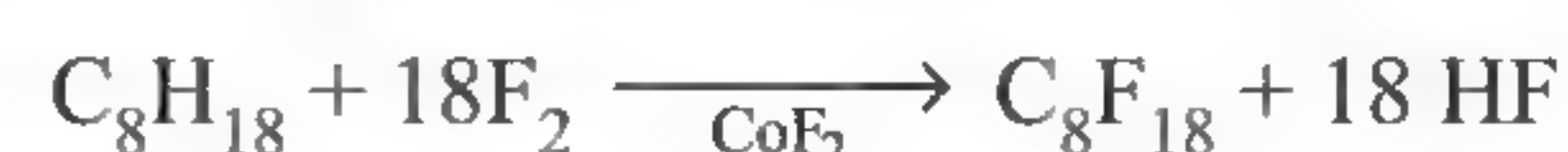
18. (1, 2, 3)

Refer to section 3.22 and 3.23.

Correct (1): It is prepared as:



Correct (2): Fluorination of octane.



Correct (3): DDT is prepared from chlorobenzene and chloral.

19. (2, 3, 4)

(1) Products would be a mixture of (I) and (II) (2), (3), (4) would

produce stable $\left(\begin{smallmatrix} \text{Me} \\ \diagup \\ \text{C}^+ \\ \diagdown \\ \text{Me} \end{smallmatrix}\right)$ carbonium ion and would yield

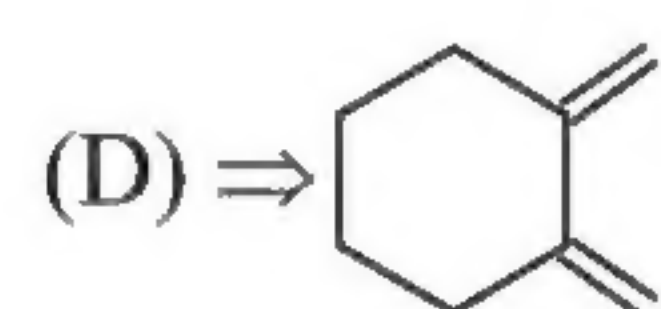
100% of cumene $\left(\text{C}_6\text{H}_5\text{CH}(\text{Me})_2\right)$.

Linked Comprehension Type

Paragraph 1

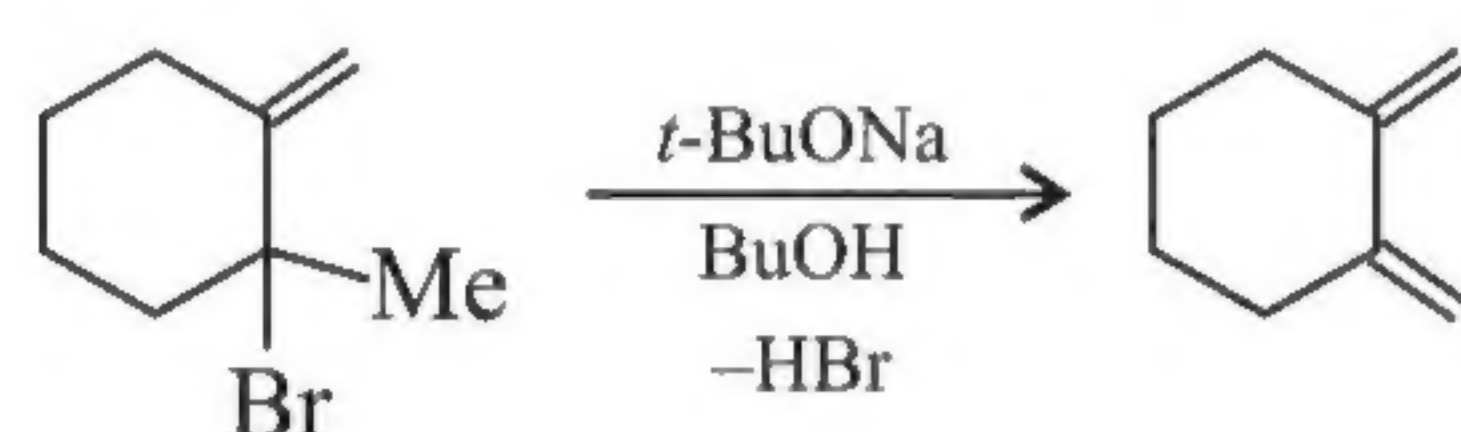
1. (1), 2. (3), 3. (2), 4. (2), 5. (2), 6. (1), 7. (4), 8. (2)

i. Proceed reverse from (E) to (D), (E) is obtained by the 1,4-addition of Br_2 on (D). (D) must be a conjugated diene.

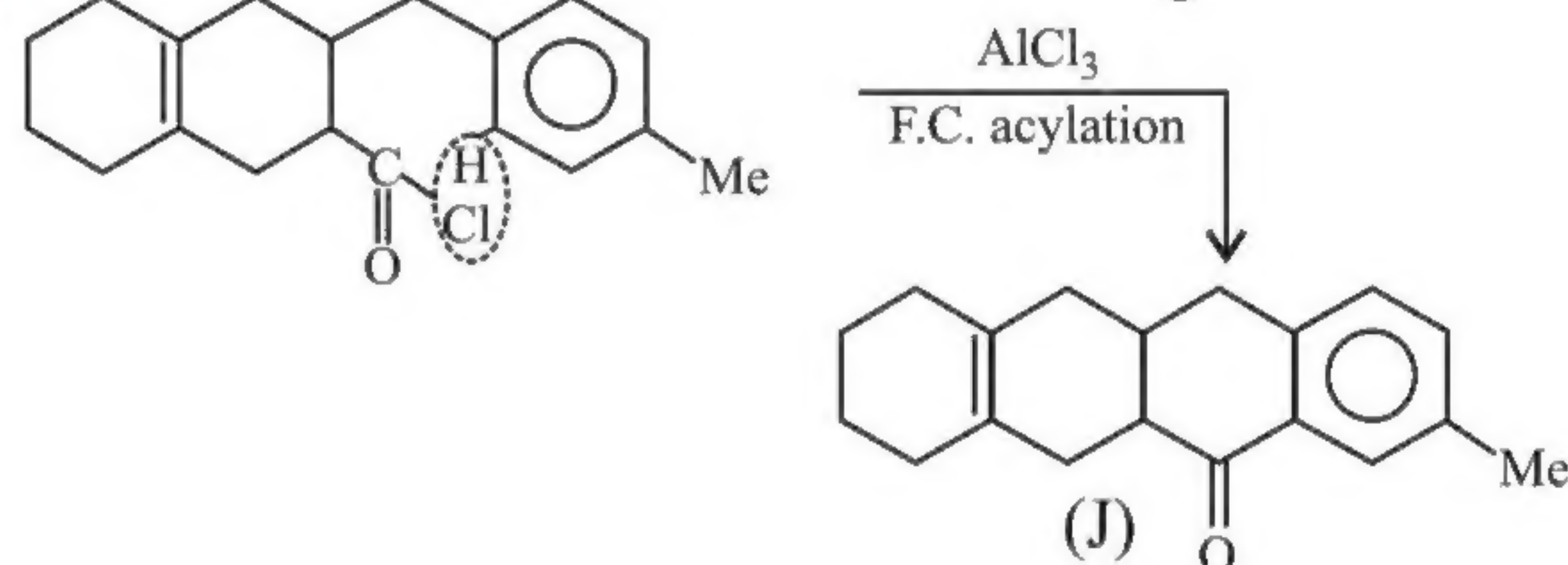
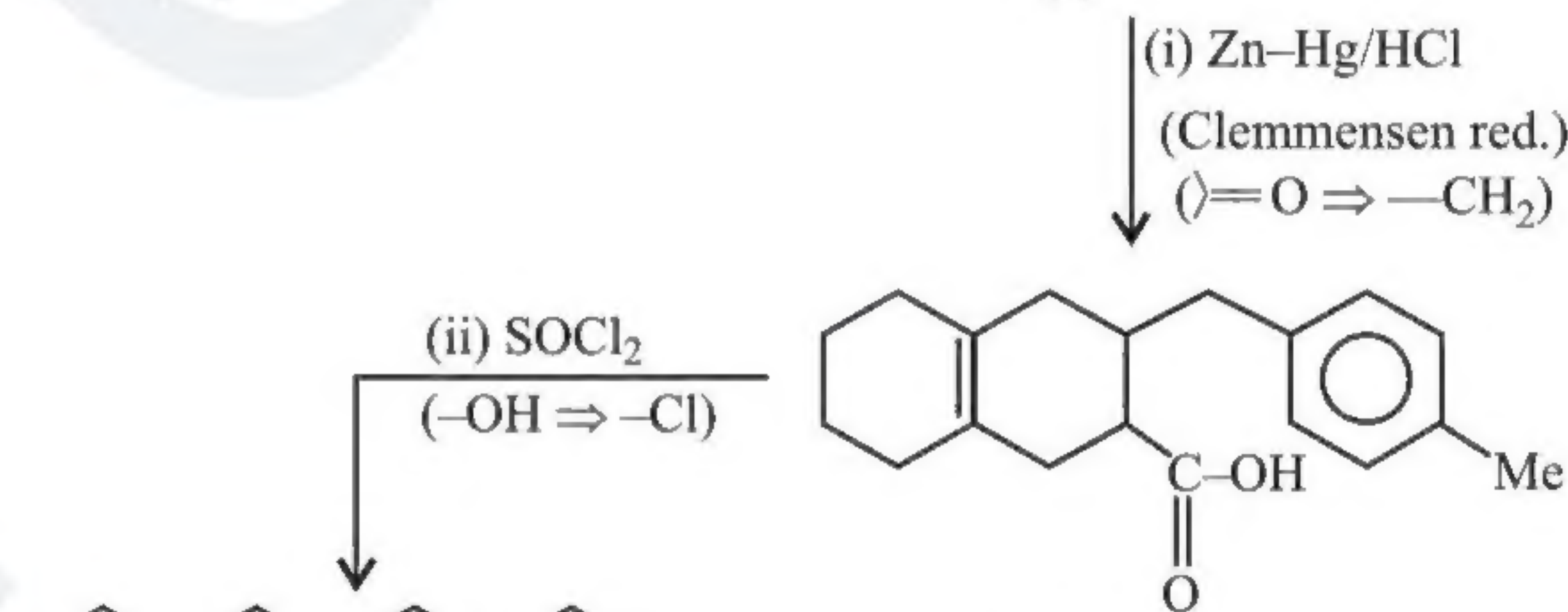
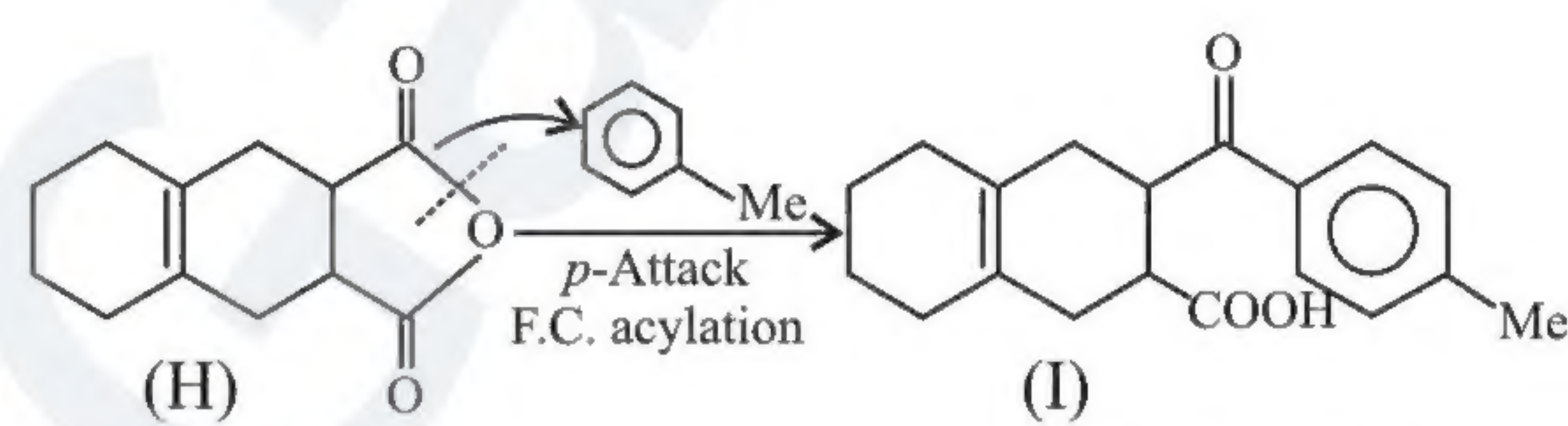
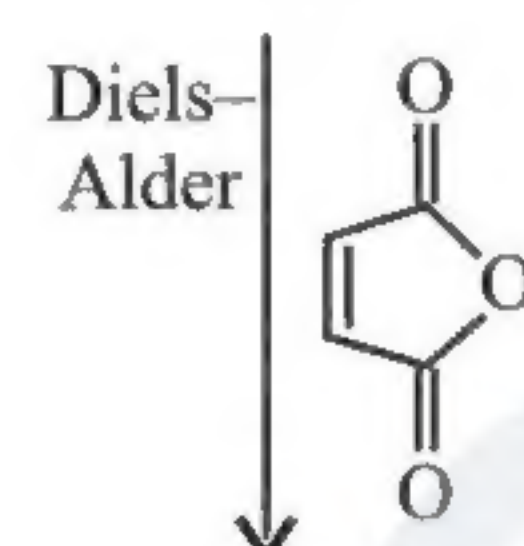
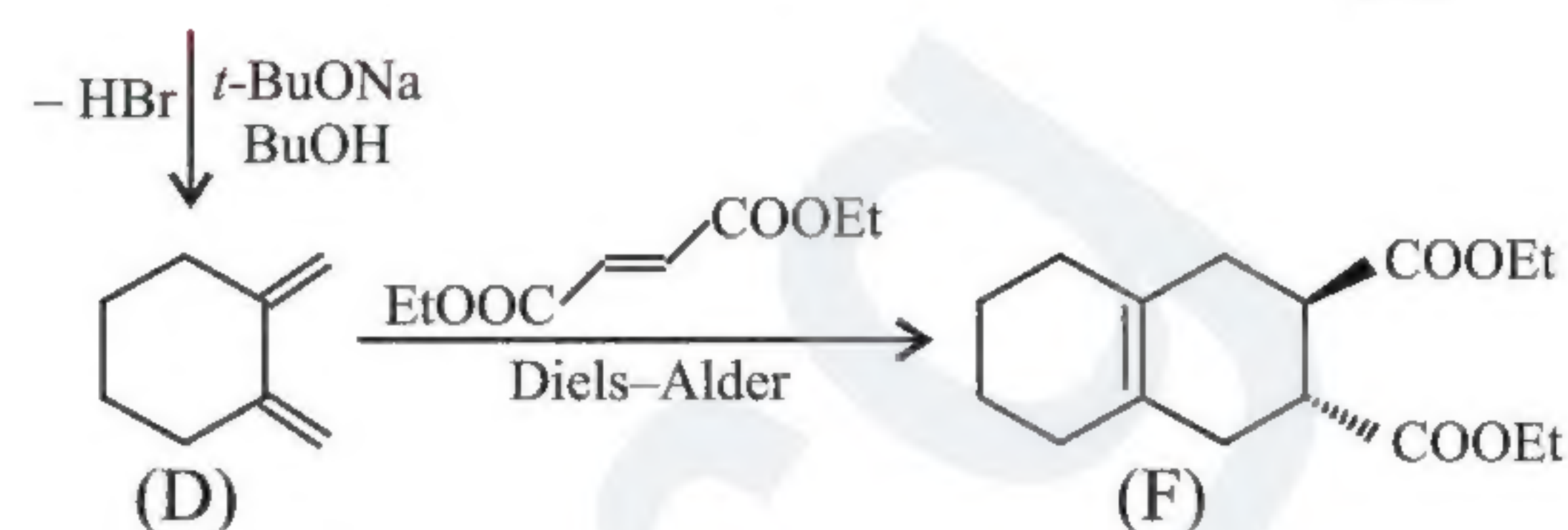
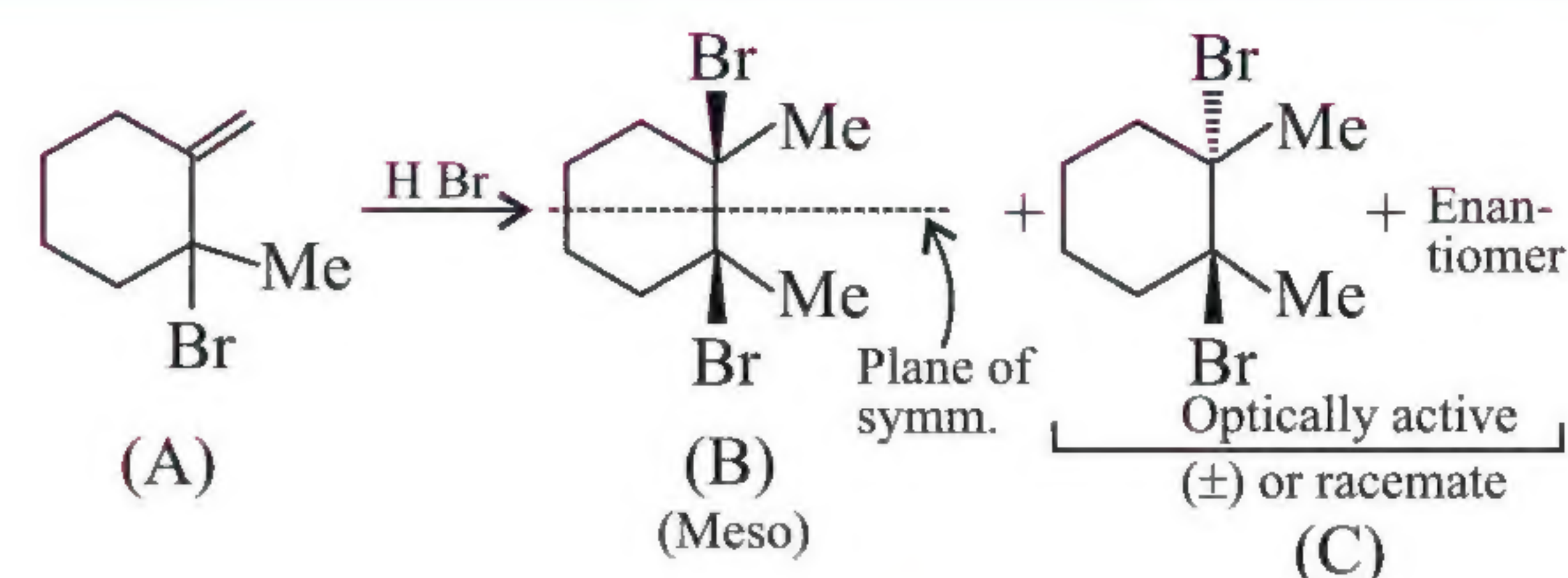


ii. (D) is obtained from (A), and (A) to (D) is elimination reaction by bulky base to give less-substituted alkene (Hofmann elimination).

So (A) is:

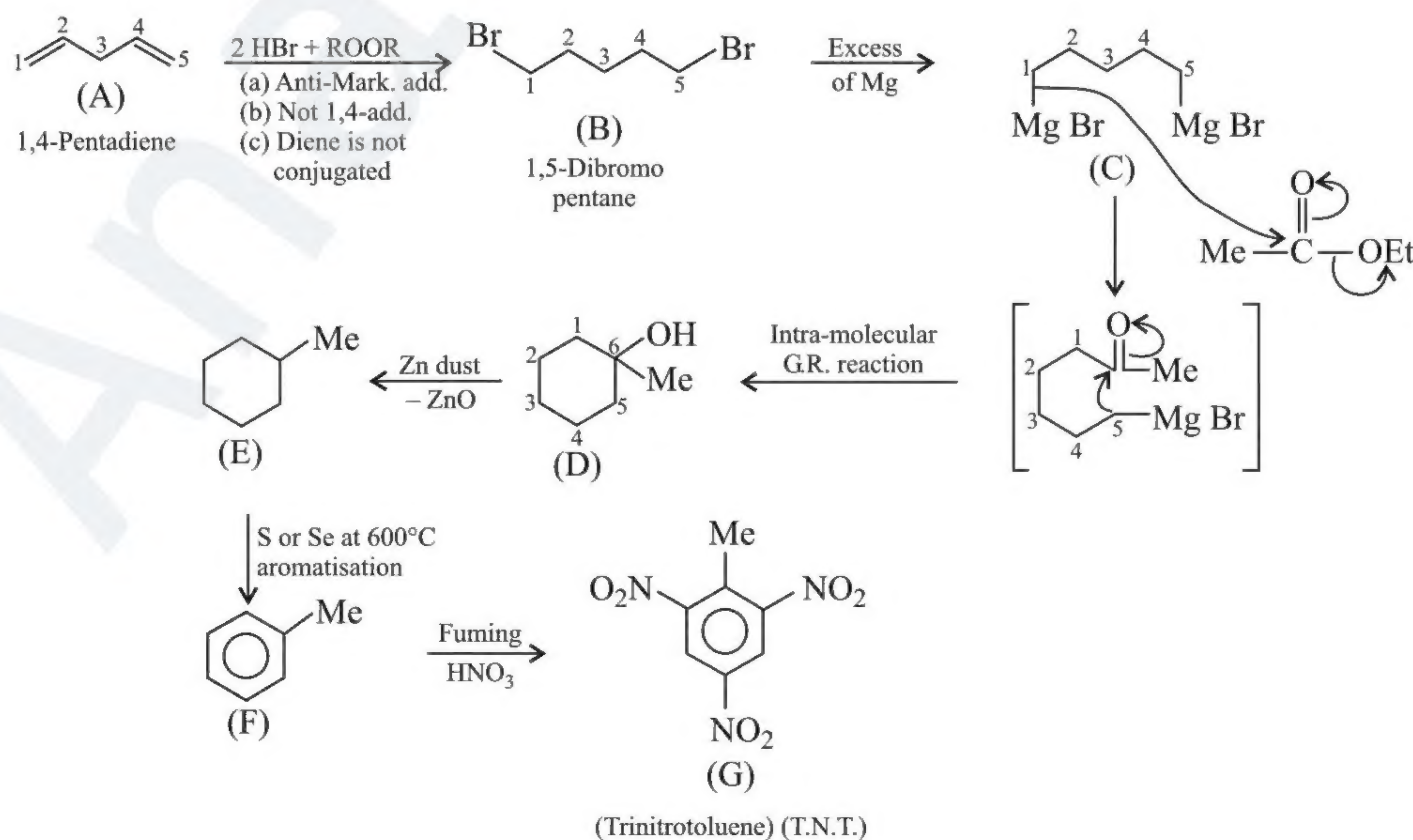


Reaction can be summarised as



Paragraph 2

9. (2), 10. (3), 11. (1), 12. (4), 13. (2)

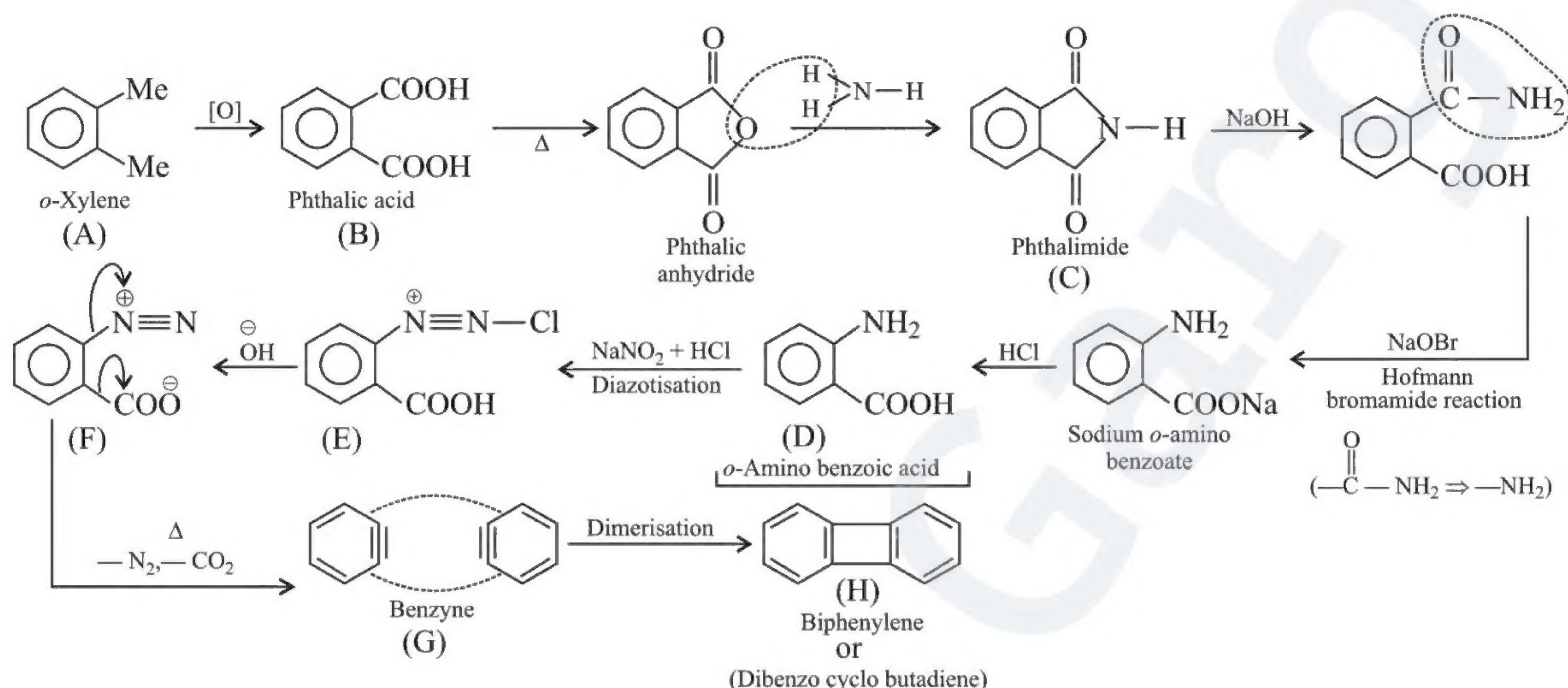


Paragraph 3

14. (4), 15. (1), 16. (3), 17. (1), 18. (2), 19. (3), 20. (2)

$$\text{D.U. in (A)} = \frac{(2n_C + 2) - n_H}{2} = \frac{(8 \times 2 + 2) - 10}{2} = 4^\circ$$

4 D.U. and C:H \approx 1:1 suggest that (A) contains benzene ring with two extra C atoms [i.e., two (Me) groups]. Since compound (A) is steam volatile and on nitration gives two nitro-derivatives, so (A) is *ortho*-xylene.

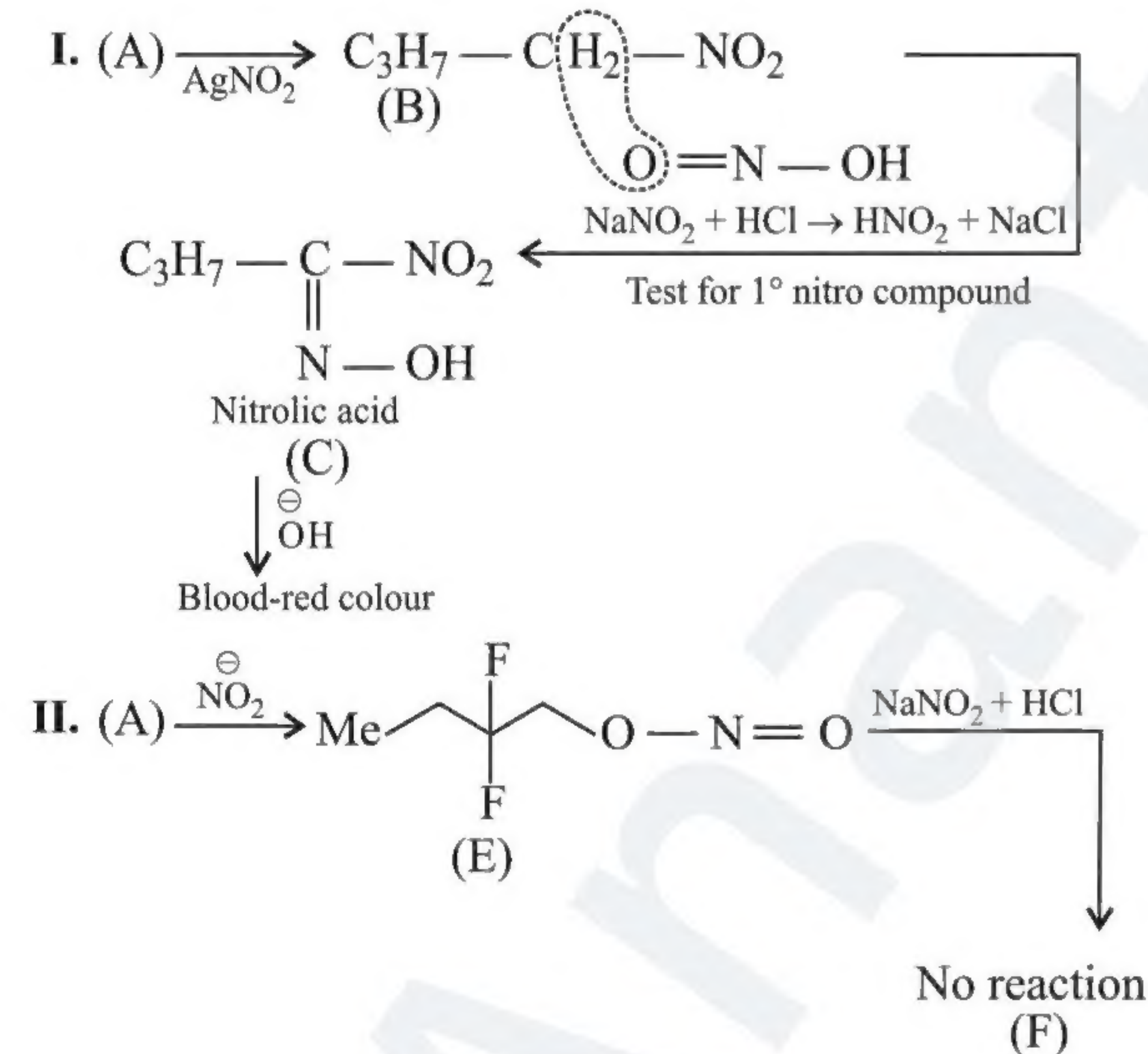


21. (3) D.U. in H = Two benzene ring + cyclobutane ring = $(2 \times 4 + 1) = 9$

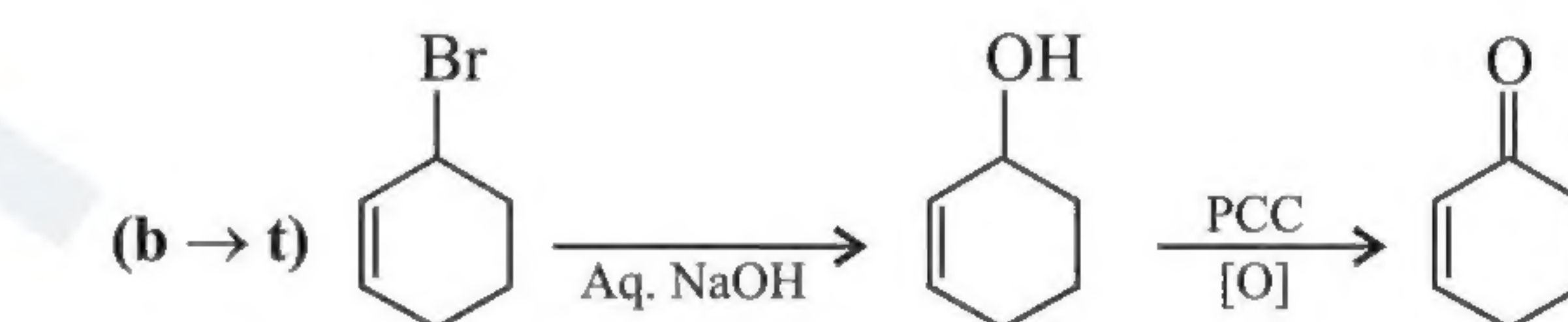
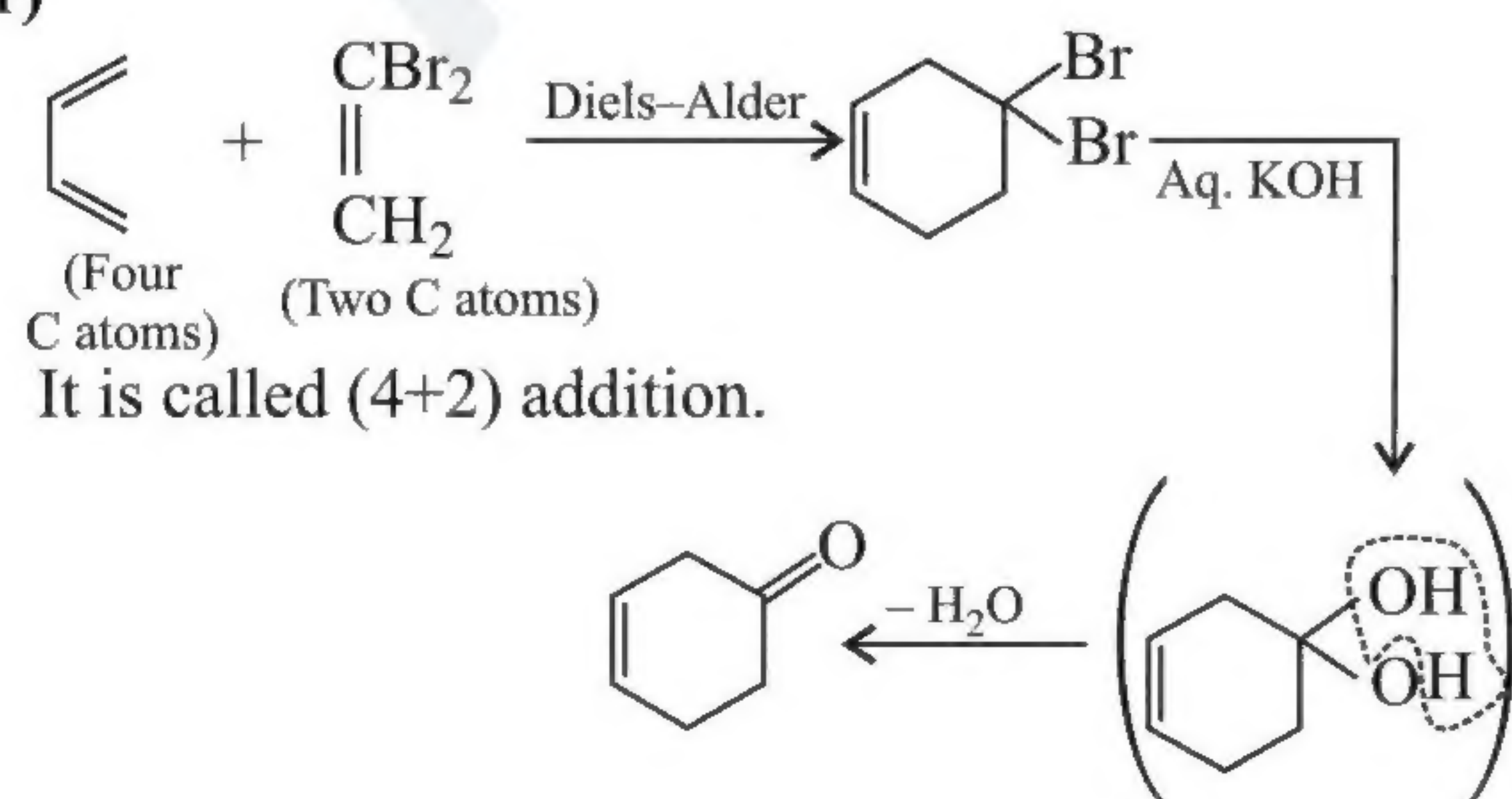
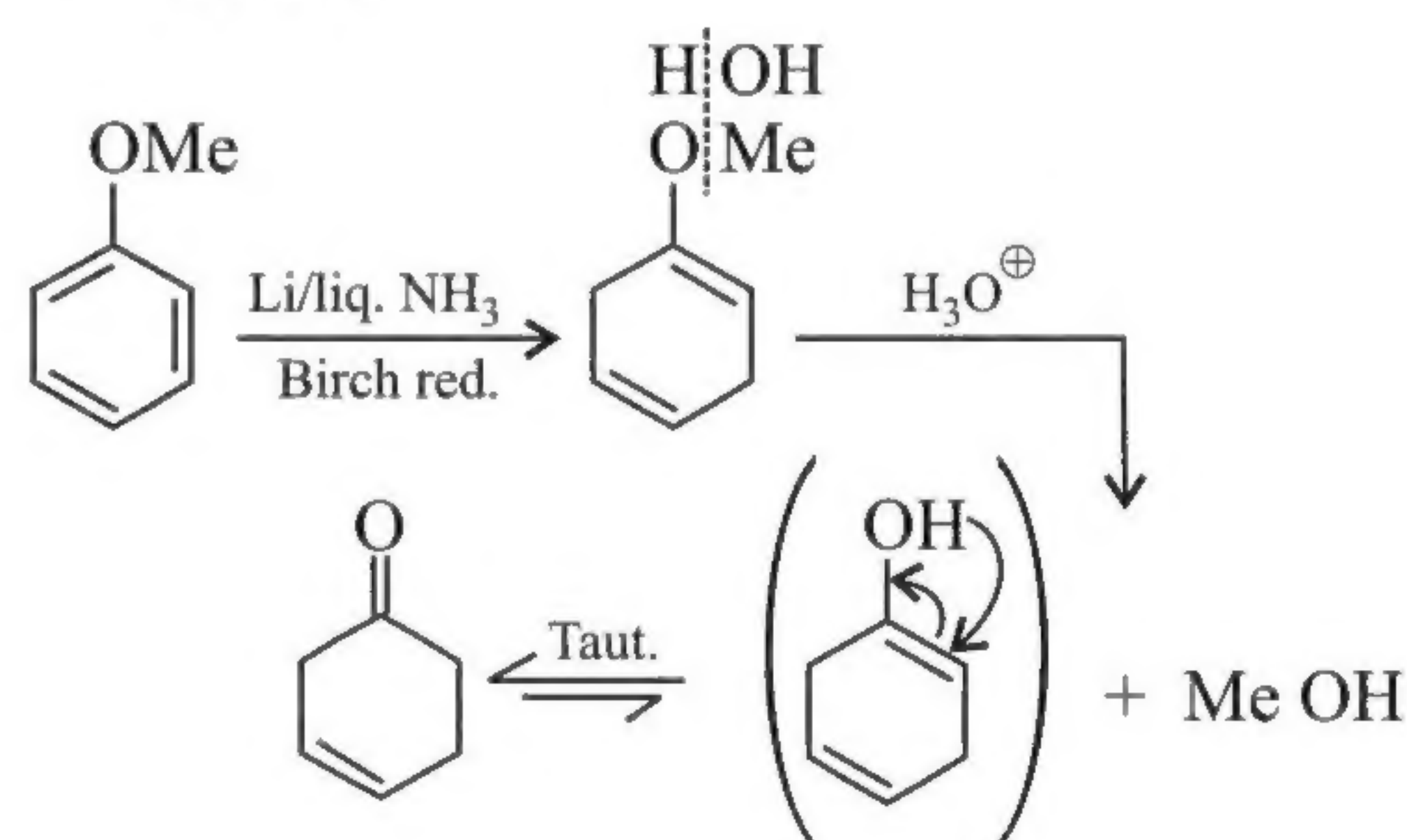
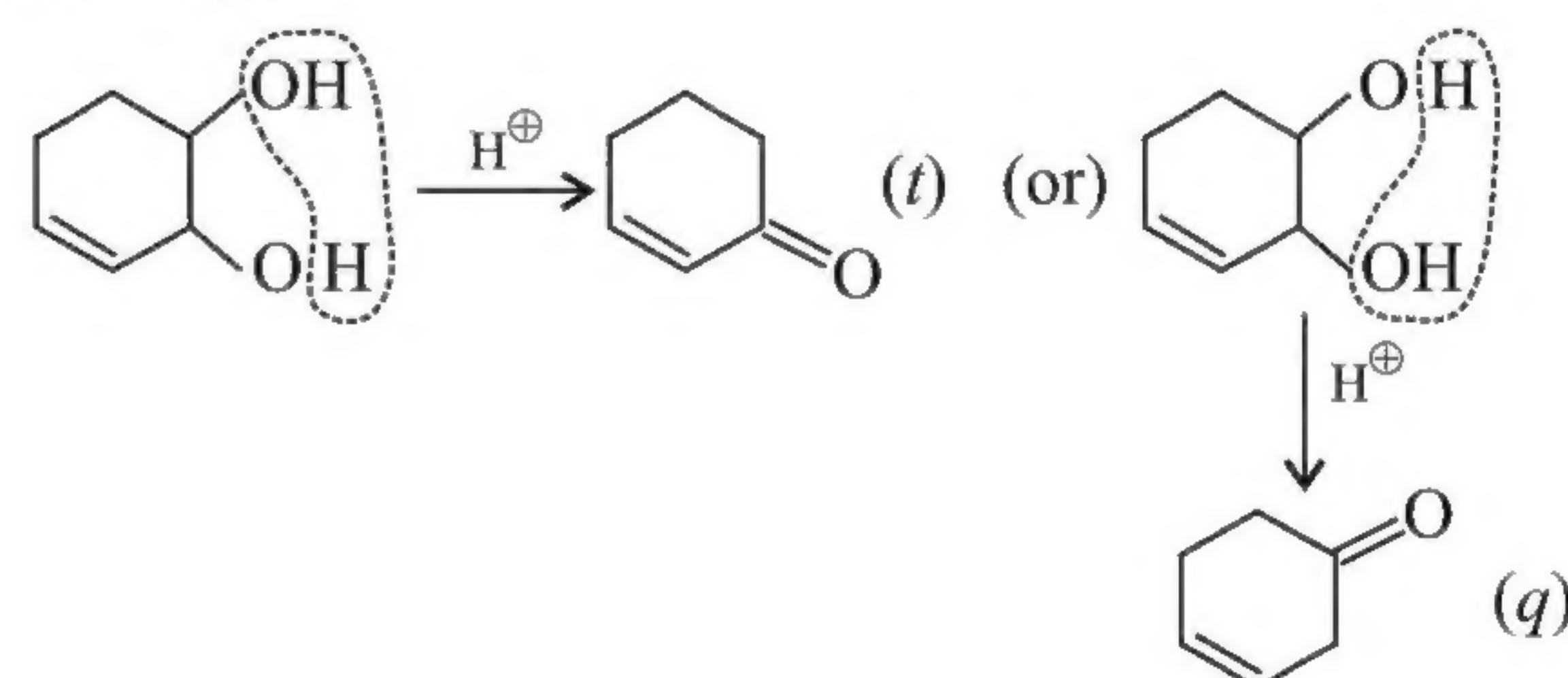
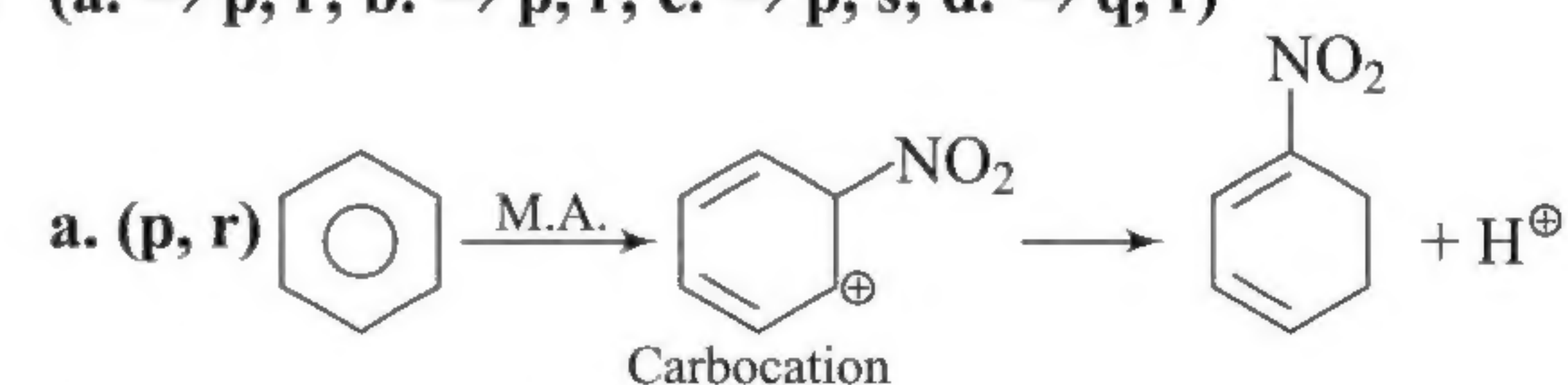
Paragraph 4

22. (1), 23. (1), 24. (2), 25. (3)

RX in (I) gives $R-NO_2$, while in (II) it gives $R-O-N=O$.

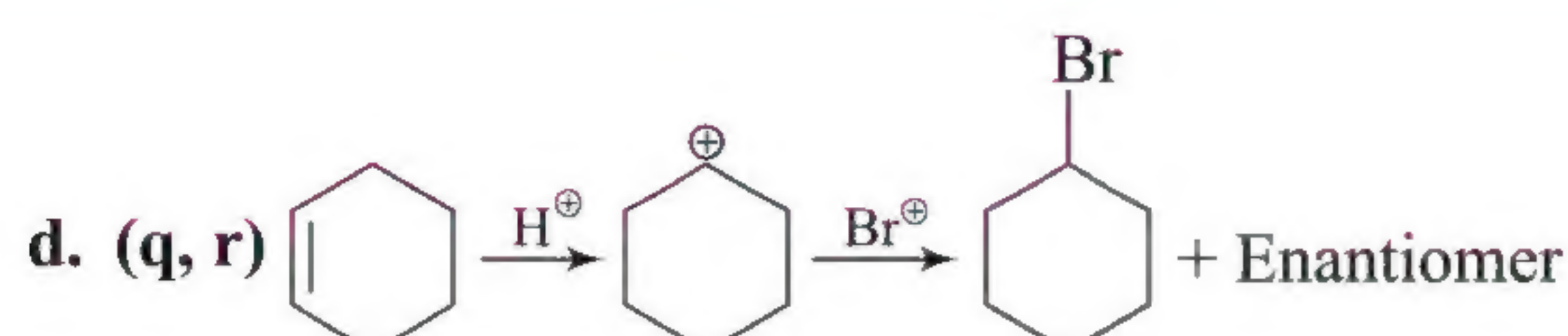


Matrix Match Type

1. (a \rightarrow q, r; b \rightarrow t; c \rightarrow p, q, s; d \rightarrow q, t)(a \rightarrow q, r)(c \rightarrow p, q, s)(d \rightarrow q, t)2. (a. \rightarrow p, r; b. \rightarrow p, r; c. \rightarrow p, s; d. \rightarrow q, r)

b. (p, r) Friedel-Crafts halogenation

c. (p, s) Aromatic nucleophilic substitution (Carbanion is intermediate)



3. (a. → p, r; b. → p, r; c. → q; d. → p)

a. (p, r.) SN^1

b. (p, r) SN^1

c. (q) Elimination

d. (p) SN^2

4. (a—iii—p; b—iv—s; c—i—q,t; d—ii—r)

a—iii—p

Refer to section 3.4.6

b—iv—s

Refer to section 3.19

c—i—q,t

d—ii—r

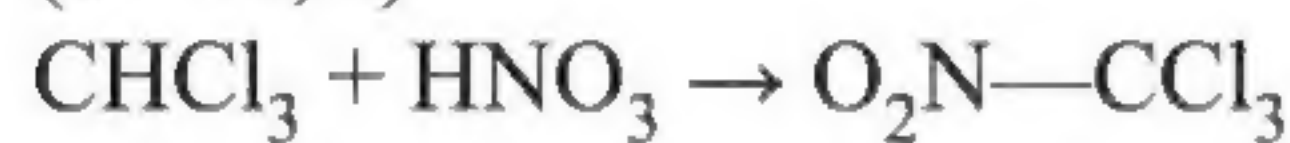
Refer to section 3.14.1 and 3.15

5. (a → r; b → s; c → t; d → u, e → v; f. → p; g → q)

6. (a → p, q, s; b → p, q, r, s; c → q, r, s)

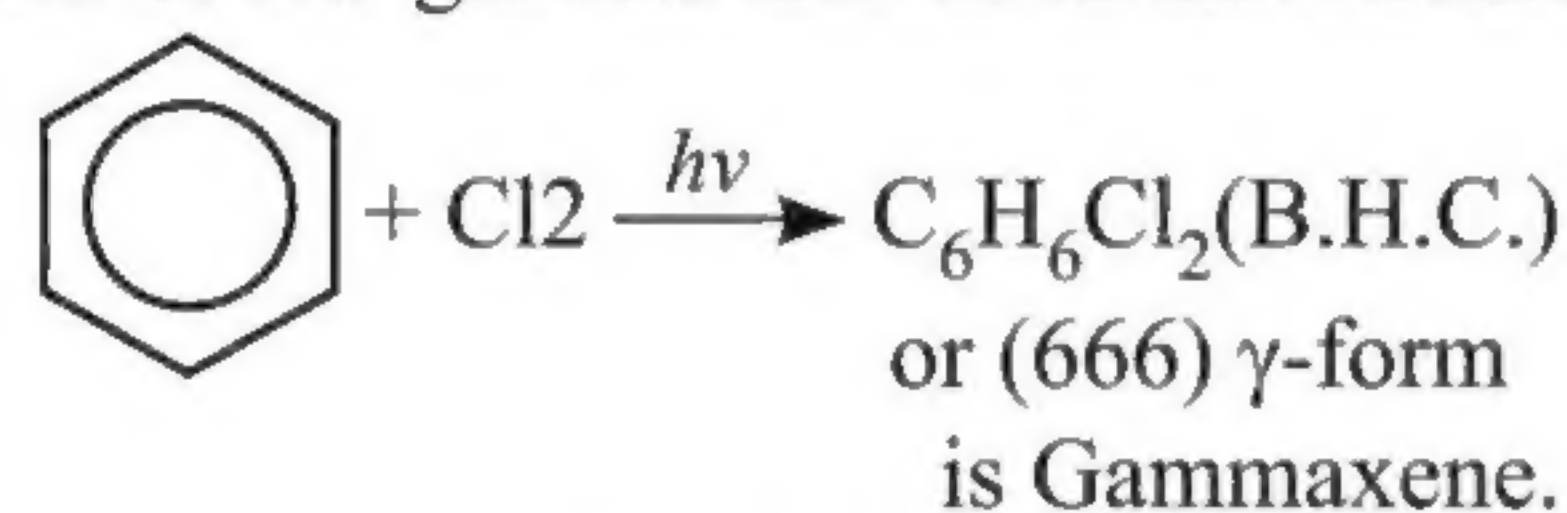
7. (a → r, s; b → p; c → t; d → q; e → u)

(a → r, s)



(Chloropicrin is used as tear gas and also as an insecticide)

(b → p)



(c → t)

Preparation of D.D.T.

(d → q)

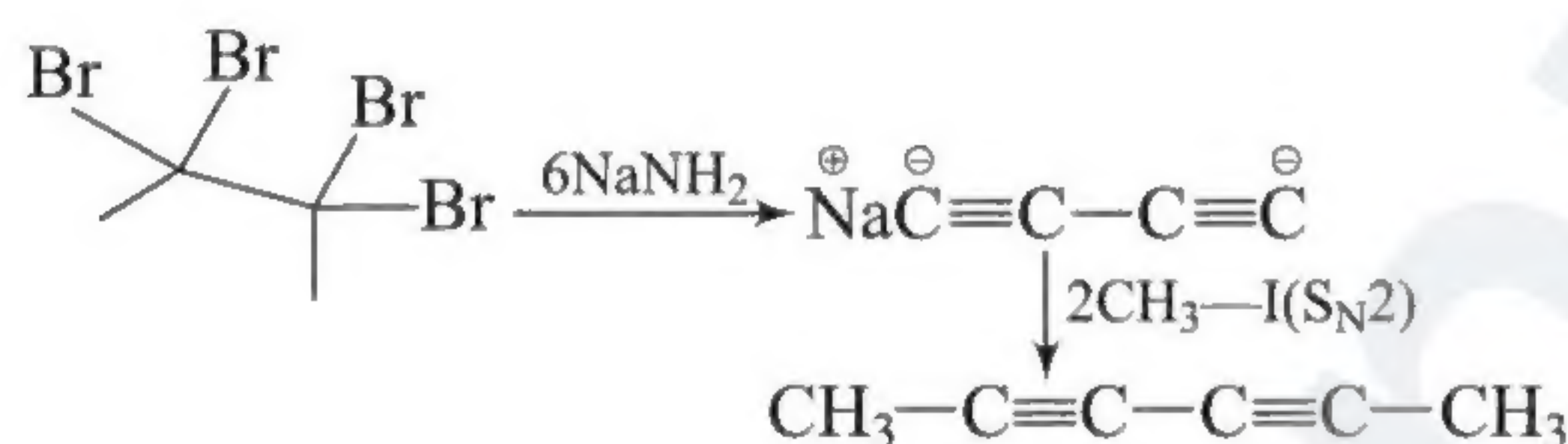
Borodin–Hunsdiecker reaction.

(e → u)

Used as weeping gas.

Numerical Value Type

1. (8)



2. (8)

A.  (3 Products)

B.  (3 Products)

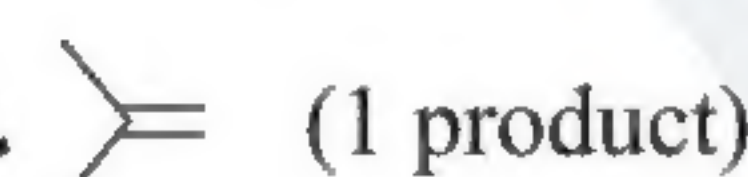
C.  (2 Products)

D. No β -hydrogen so no E2 reaction

$$\therefore A + B + C + D = 3 + 3 + 2 + 0 = 8$$

3. (9)

A.  (3 products)

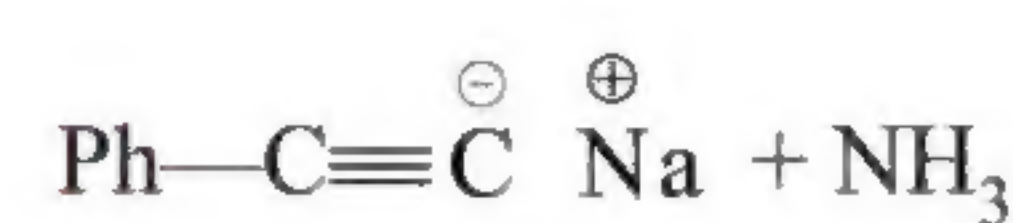
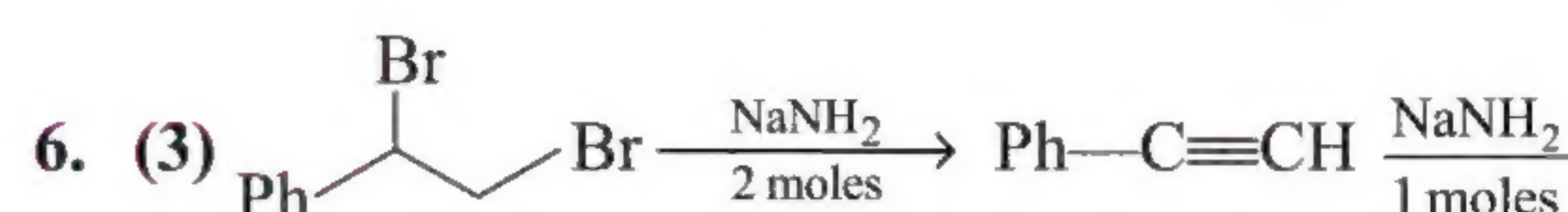
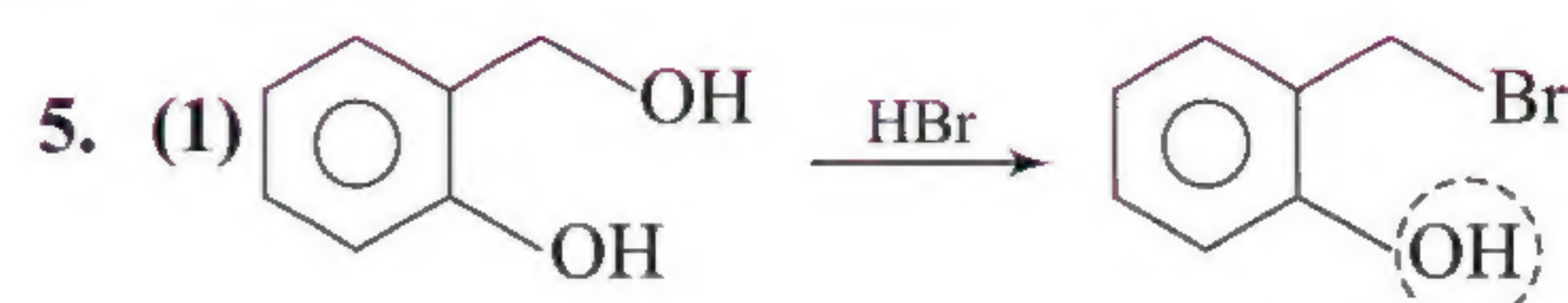
B.  (1 product)

C.  (3 products)

D.  (2 products)

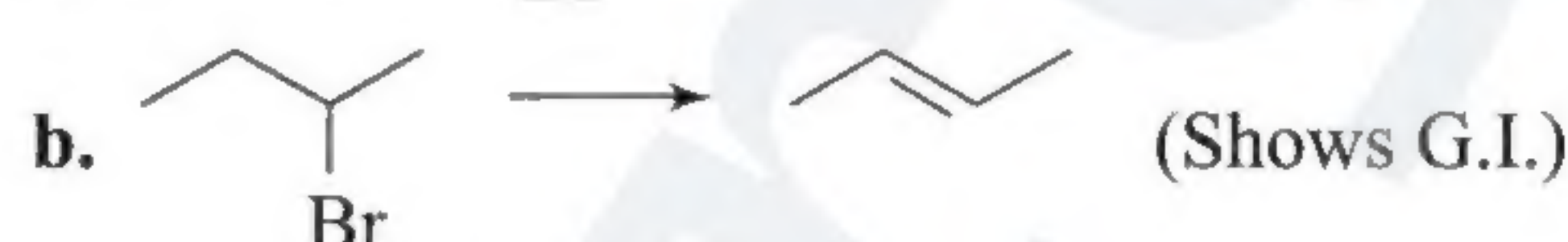
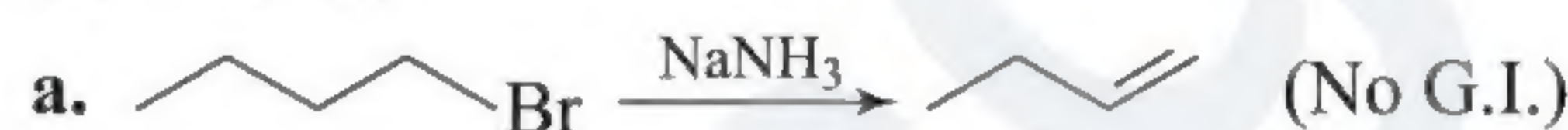
$$\therefore A + B + C + D = 3 + 1 + 3 + 2 = 9$$

4. (2) For Anti elimination H and Cl must be in anti-position, only two moles of HCl are in anti position.

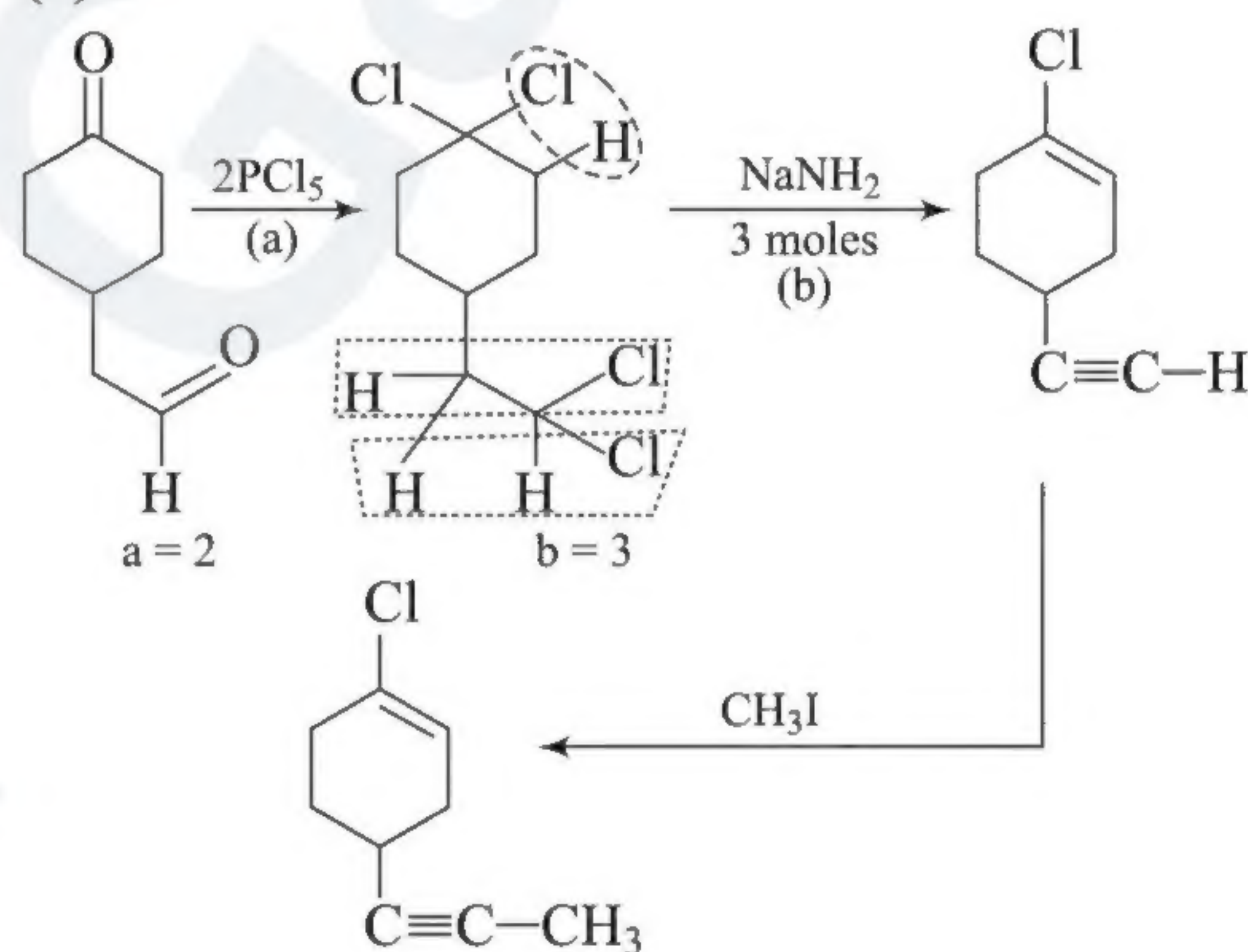


$$(X) = 2 + 1 = 3 \text{ moles}$$

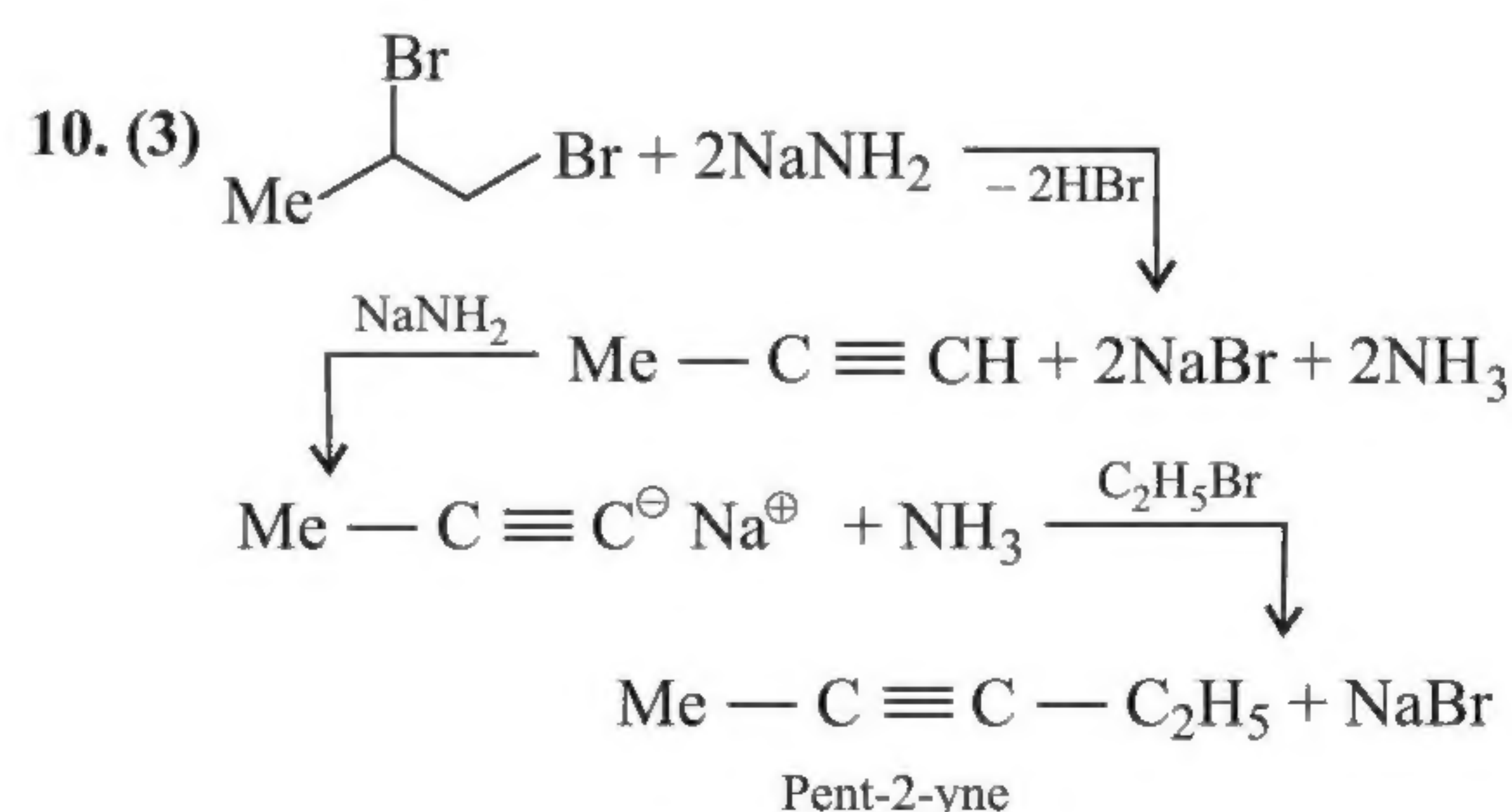
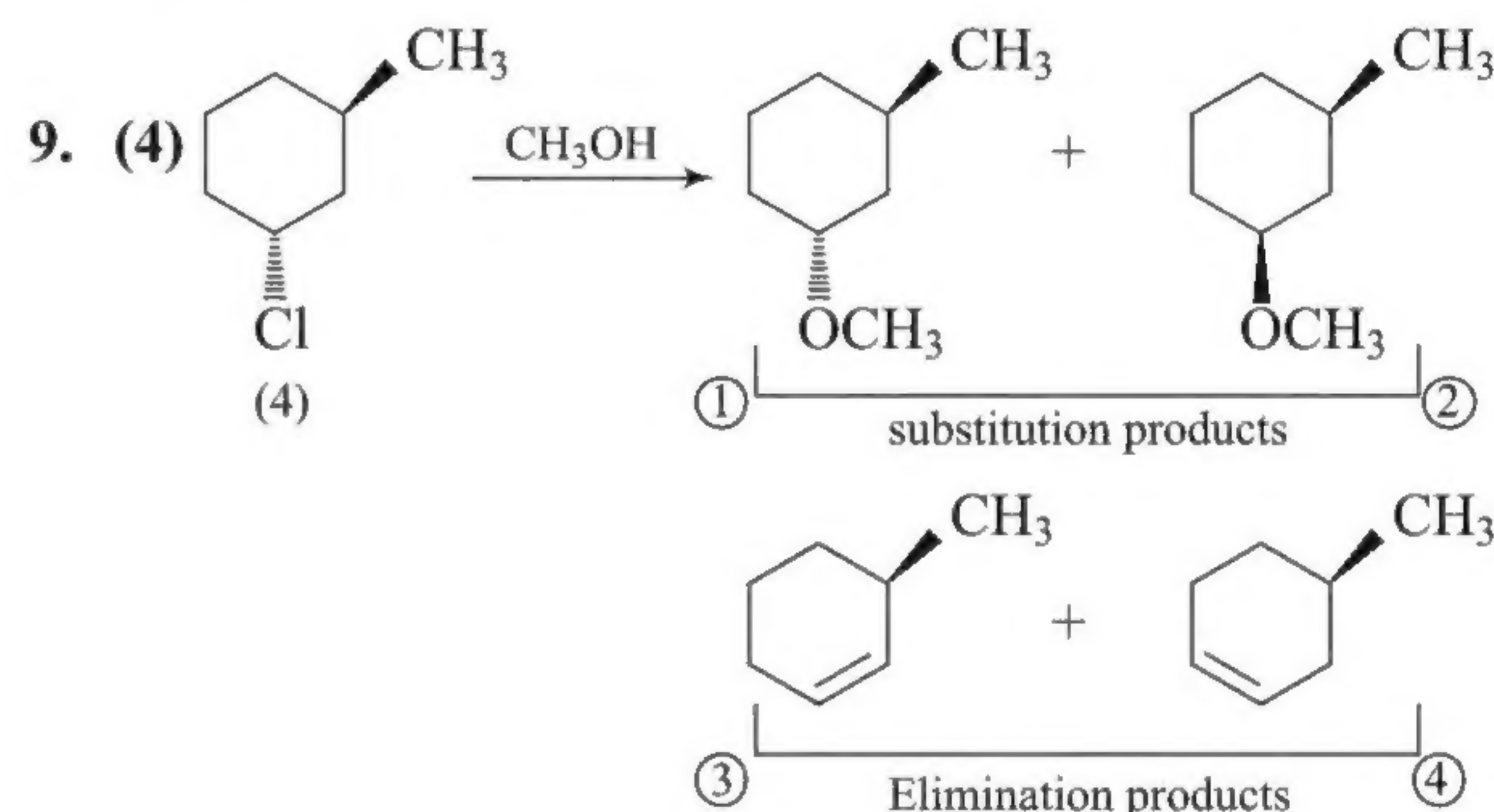
7. (1) Only (b) diastereomers



8. (5)



$$\therefore a + b = 5$$

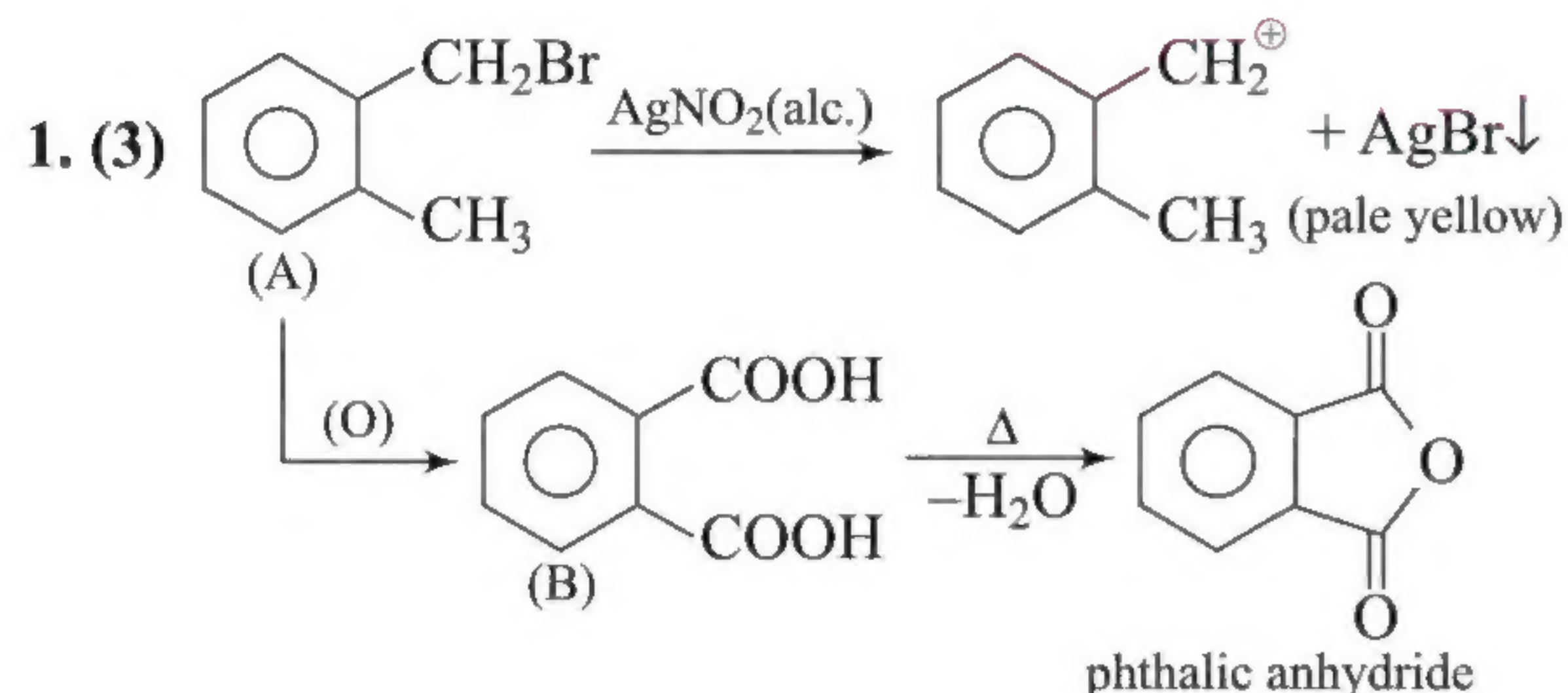


Hence, 3 mol $NaNH_2$ is used.

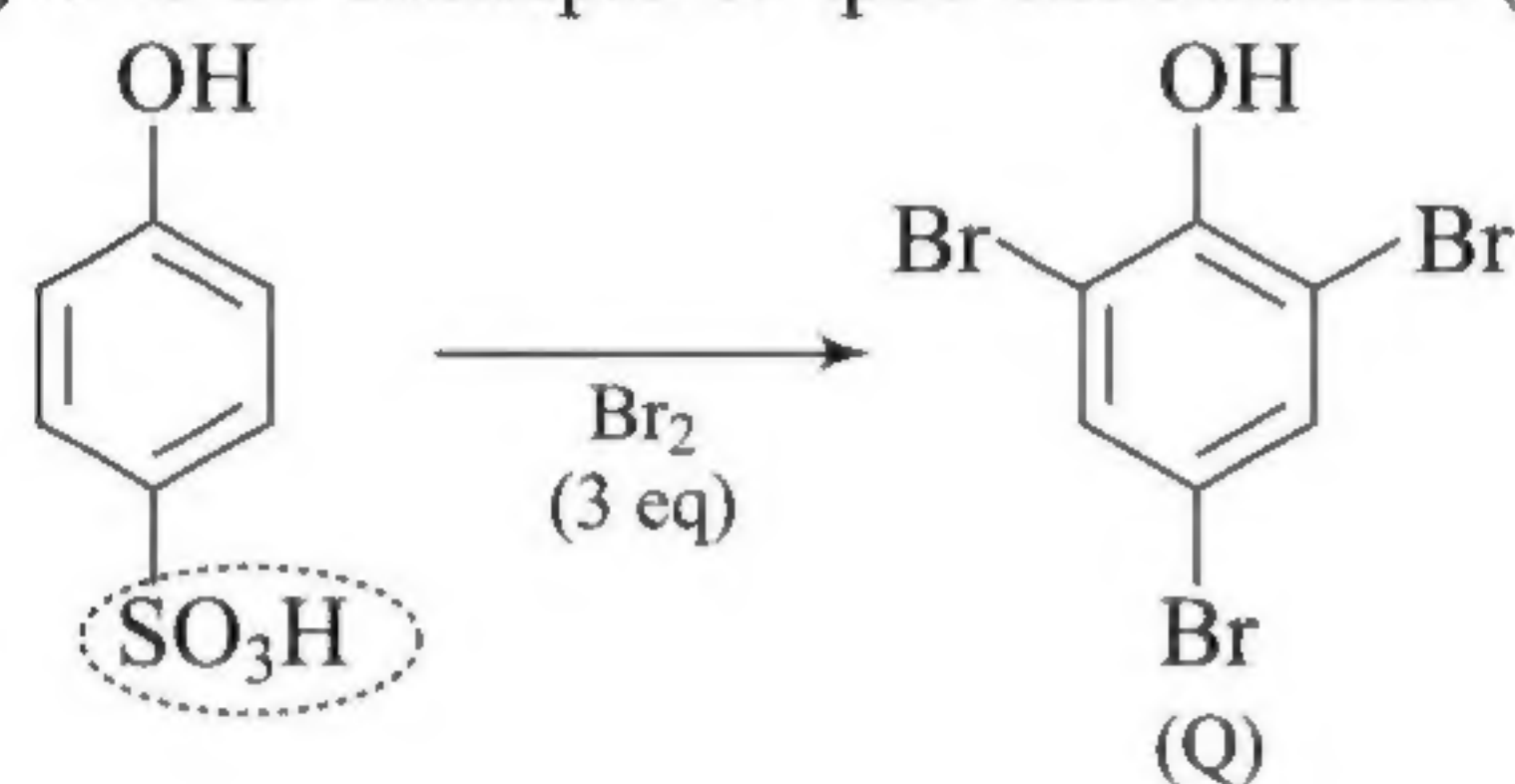
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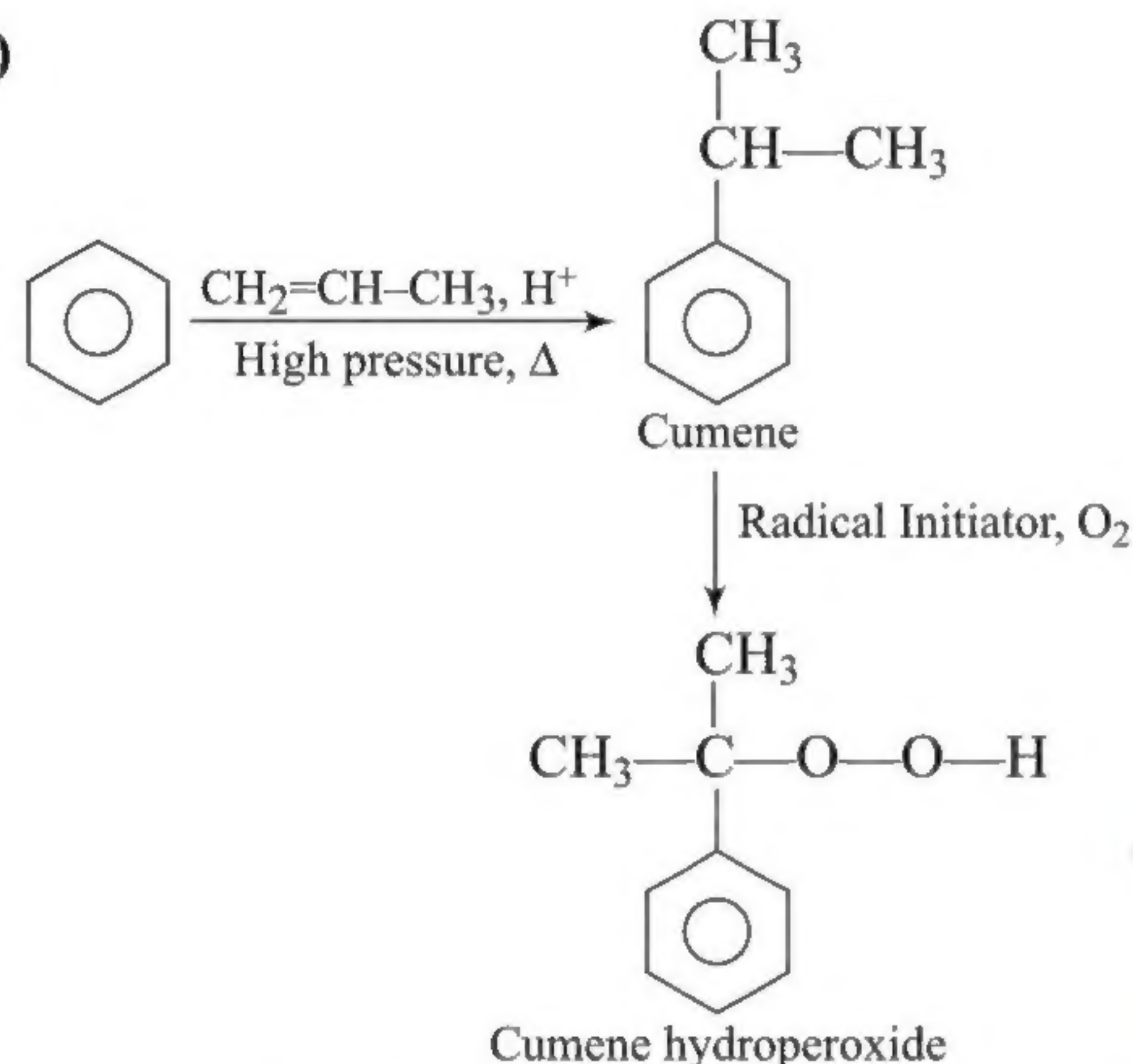
Single Correct Answer Type



2. (2) It is an example of ipso substitution (Refer Section 3.15)



3. (2)

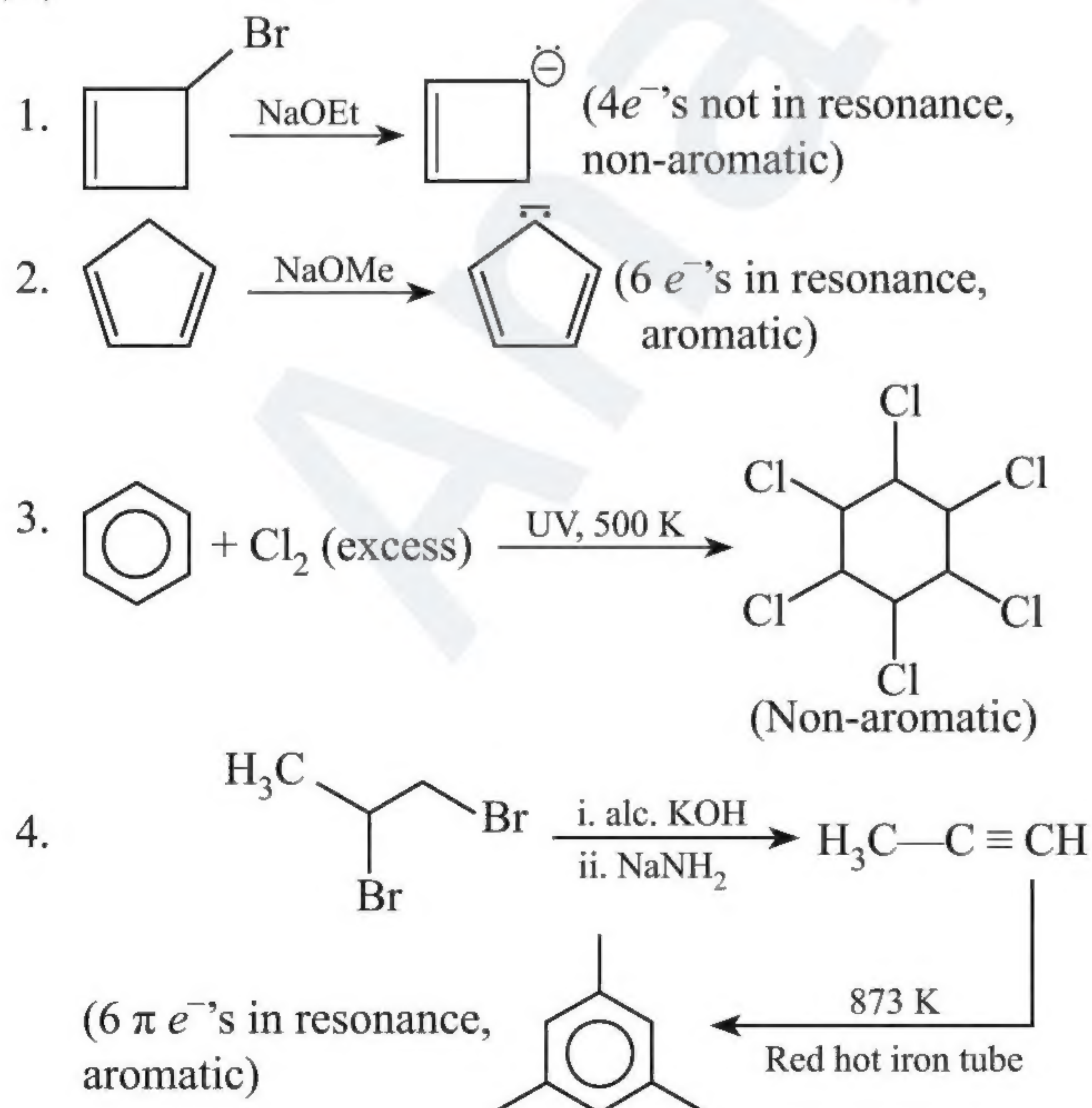


4. (4) $\text{R-I} + \text{AgF} \rightarrow \text{R-F} + \text{Ag I}$ (Swarts Reaction)

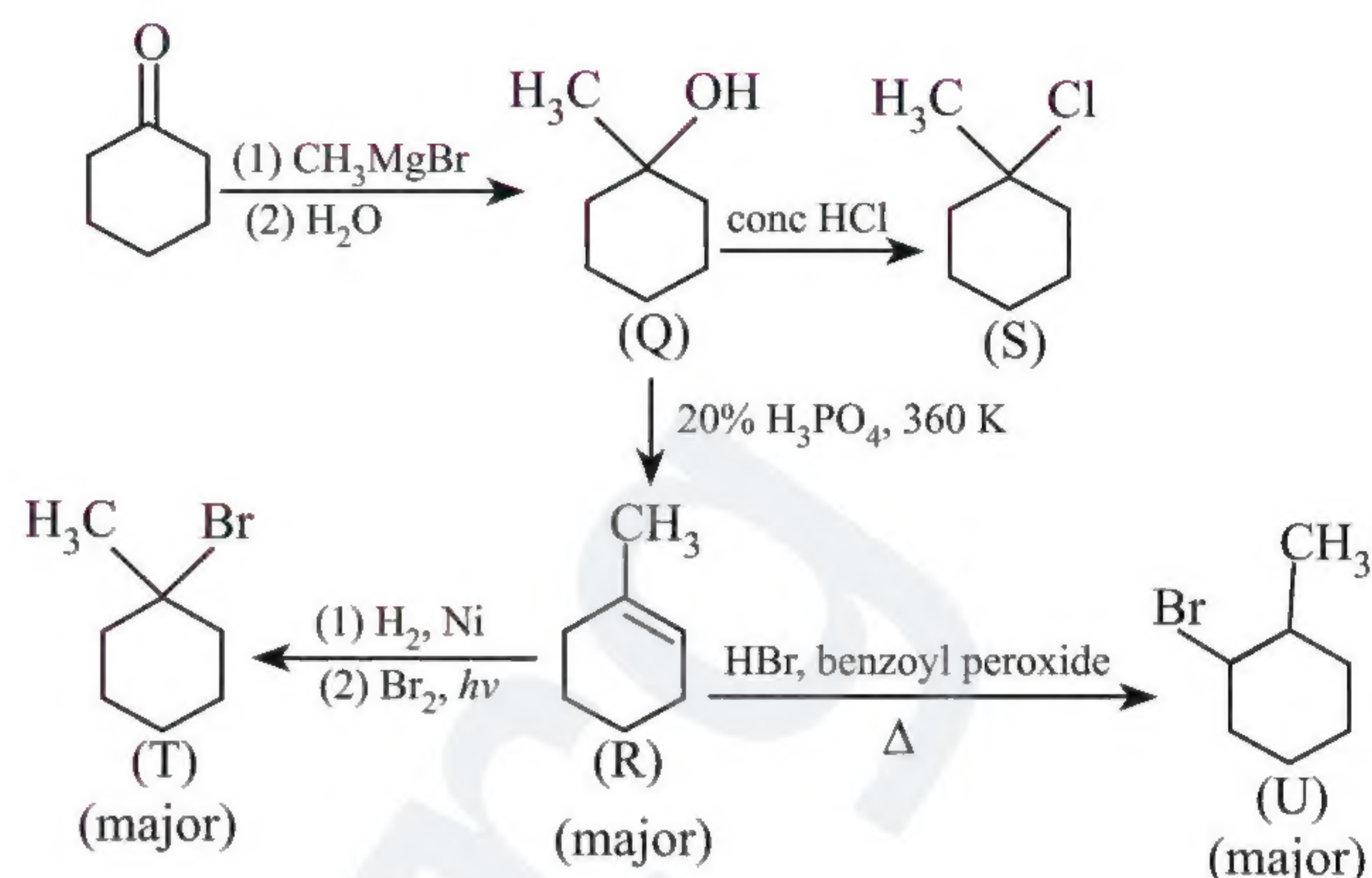
Multiple Correct Answers Type

1. (1, 2, 3) Factual statement

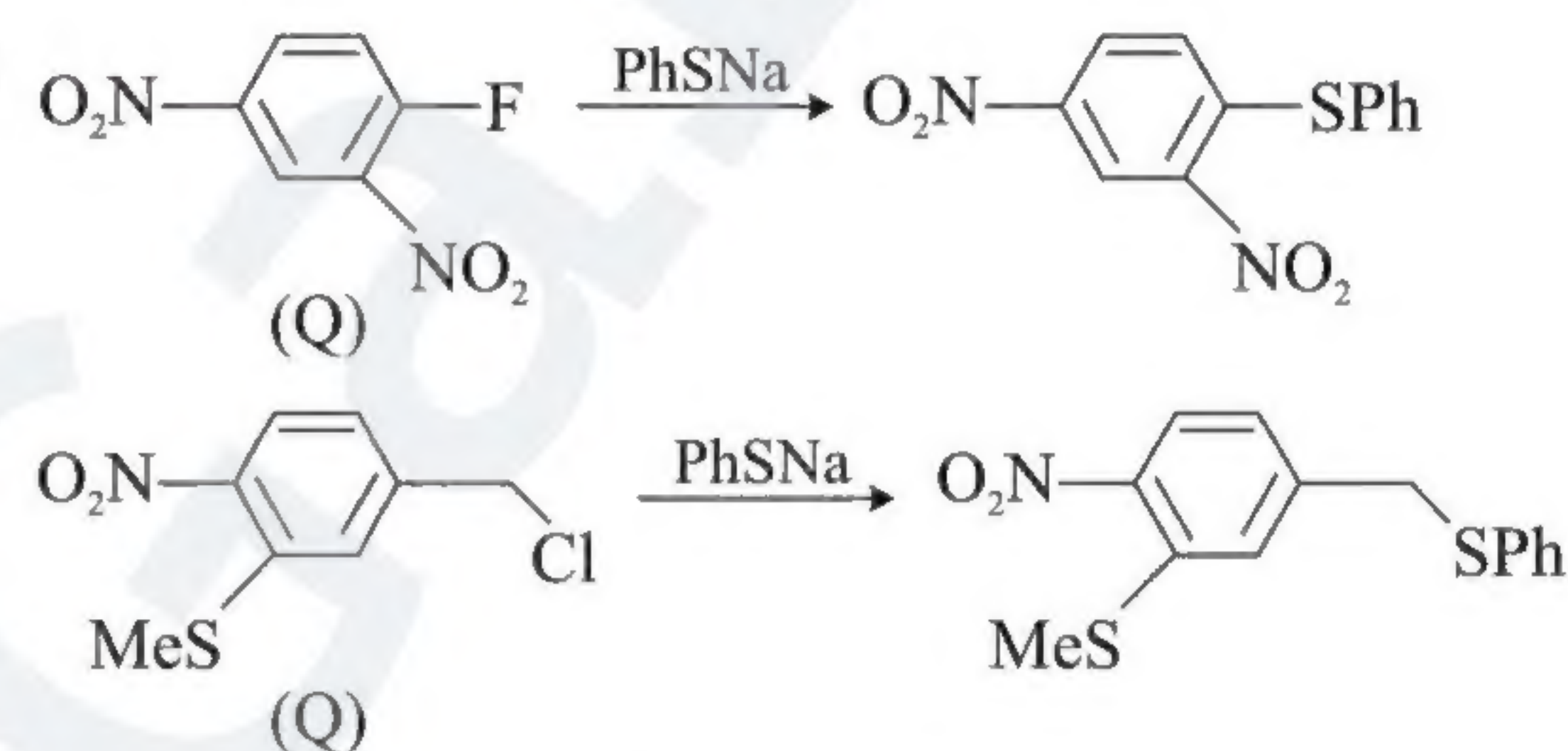
2. (2, 4)



3. (3, 4)



4. (1, 4)



Both the products have sulphur, so they give positive carius test on treatment with Na_2O_2 by BaCl_2

Linked Comprehension Type

1. (2)

2. (4)

